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# SOIL SCIENCE

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# RELATION OF pH DRIFT TO MOISTURE CONTENT AND BASE HELD IN SOILS

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This paper deals with a study of the pH values and their drift, in soils at various soil-water ratios as affected by exchangeable bases and water content of soils, when measured by the quinhydrone electrode.

There has been much discussion concerning the determination of hydrogen-ion concentration of soils by the quinhydrone electrode. In certain soils a decided drift of pH with time is found to occur when determinations are made by this method. The International Society of Soil Science (4) has studied the problem, the studies being made in part on account of the report by Kühn (9), who suggested that soil investigators give up the quinhydrone electrode and use the indicator method. Kühn finds many soils whose pH value as measured by the quinhydrone electrode will vary as much as 0.5 units in one and a quarter minutes. Biilmann and Tovborg-Jensen (1) found no appreciable drift of potential between the readings of one-half minute, fifteen minutes, and four hours after the addition of quinhydrone. Heintze and Crowther (7) suggest that an active form of manganese dioxide in intimate association with soil colloids might cause an error in the determination of soil reaction by the quinhydrone electrode, due to the reduction of manganese dioxide to manganous hydroxide. McGeorge (10) concludes that the accuracy of the quinhydrone electrode for the determination of soil reactions is greatly affected by the presence of small amounts of manganese dioxide; but does not condemn the method, as the drift shown by the potentiometer is sufficiently rapid to warn the analyst. Brioux and Pien (2) found abnormal values by the quinhydrone electrode for soils overlying chalk. Among others Heintze and Crowther (7) report that Christensen and Tovborg-Jensen (3) find that laterite soils give high pH values by the quinhydrone electrode. It is well known that the quinhydrone electrode is not accurate for solutions more alkaline than about pH 8.5.

That soils possess the capacity to hold and exchange bases has been well established by the work of Gedroiz (6). He also shows that soils holding a particular base exhibit notably individual physical characteristics, giving tables which show that air-dry soils saturated with various bases will take up water

[1] Contribution no. 158, department of chemistry.

and increase their volume by various amounts. Thus soils saturated with sodium will swell 47 per cent while soils holding ammonium, potassium, calcium, aluminum, and ferric iron will swell 24, 19, 17, 6, and 4 per cent, respectively. The amount of water held by the various soils at complete saturation with water in grams per 100 gms. soil in sodium 106, ammonium 78, potassium 73, calcium 71, aluminum 63, and iron 51. Smolik (13) found that soil samples saturated individually with sodium, calcium, magnesium, potassium, and ammonium held water in decreasing order of magnitude. The authors also found that the base held by a soil had considerable effect on its capacity to hold water. These variations are taken up under the heading of "The Soils Used."

In studying the problem of potential drift the International Society of Soil Science (5) reports that of 28 soils studied 20 gave pH values obtained by the quinhydrone electrode comparable to those obtained by the hydrogen electrode. The other eight soils showed a decided drift of potential when the quinhydrone electrode was used. A study of the report shows that the drift probably consists of two parts: first, a rapid drift for about 60 seconds after the addition of the quinhydrone and, second, a slower drift over a longer period of time. Fifteen minutes was the maximum time for which the drift was studied.

## THE PROBLEM

With the facts of base exchange, altered physical characteristics of the soil as governed by exchangeable base, and drift of pH of soils obtained under various conditions the authors decided to investigate the effect of exchangeable base on potential drift. The bases used in treating the soils were sodium, potassium, ammonium, hydrogen, calcium, magnesium, aluminum, and ferric iron. In conjunction with these studies it was decided to make the reaction determinations on soils dried over calcium chloride and on soils saturated with water by keeping them over water. The measurements were made at soil-water ratios of 1–1, 1–2.5, 1–10, and 1–100. The ratio of 1–2.5 is probably the one most commonly used in soil investigations.

## APPARATUS USED AND TECHNIQUE

In general the apparatus and technique used is that given by the International Society of Soil Science (4). The platinum electrode used was heavy platinum wire of 1.5 mm. diameter, which was somewhat flattened out at the end or bent over. Thus a strong electrode is obtained of about 1 sq. cm. surface without mercury contact, and the frailty of a glass tube is avoided. Morgan, Lammert, and Campbell (11) recommend an electrode of at least 1 sq. cm. surface. The electrode vessels used were glass vials 1.5 cm. in diameter by 6 cm. in length. The potentiometric outfit used balances current resistance drop taken from an Edison cell against the E.M.F. of the electrode system, the E.M.F. being measured by a voltmeter readable to 0.001 volt. The galvanometer used as a null point indicator was sensitive to 0.025 of a micro ampere. The soil and water were mixed and then the quinhydrone was added. The

mixture was shaken vigorously for a few seconds before the electrode was inserted. The mixture was then stirred with the electrode for about 10 seconds and the first reading taken 30 seconds after the addition of the quinhydrone. To eliminate the effects of sedimentation the mixture was always restirred immediately before a reading was taken. Measurements were made in the presence of air. Numerous measurements were made under a stream of hydrogen, the hydrogen being led to the surface of the soil-water suspension and not into it. Thus contact with the air and adsorption of $CO_2$ were avoided but the suspension was not stirred by the hydrogen, as it is considered that a stream of hydrogen through the soil will drive out the carbon dioxide naturally occurring therein. Under these conditions the drift was approximately the same as in the presence of air. The water used in making the dilutions was $CO_2$ free, being distilled from a mixture of sodium hydroxide and potassium permanganate. The first portion of the condensate was discarded.

## THE SOILS USED

Six surface soils were selected for this work. These soils, which have been described in detail by Perkins and King (12), are mineral soils obtained in the southeastern and central eastern portions of Kansas. The original soils are somewhat acid in nature. The finer portions only of the soils have been used, a rough separation having been made by sedimentation so that only the portions most active in base exchange were retained. The soils were treated with normal chloride solutions of sodium, potassium, ammonium, calcium, magnesium, ferric iron, and aluminum, and twentieth normal hydrogen chloride. The treatments were continued until no further base exchange phenomena were evident. The soils were then washed with water and alcohol until practically free from excess electrolyte. That the soils treated as aforementioned are saturated with the various bases to the same degree is not maintained, as the unneutralized chloride solutions were used in exchanging the bases and there was a chance for hydrogen ions to be present as a result of hydrolysis when washing. However, the soils were saturated with the particular base to a far greater degree than natural soils would be.

The soils thus treated were air-dried for a period of six months and then subdivided, portions being placed in desiccators over water (in the presence of air) and other portions over calcium chloride. The desiccators were then placed in a room fairly well insulated against temperature changes and kept there until the weight of the soil indicated that equilibrium in regard to absorption or loss of water had been reached. A period of six months was required. The water-holding capacity of the soils as determined by adding the water loss of the desiccated soils to the moisture gained by the soils held in water vapor varied. The average water-holding capacity in per cent of desiccated soil for the soils treated with various bases was: Fe 22, H 23, Mg 25, Ca 30, $NH_4$ 33, Al 33, Na 39, and K 41.

## pH DRIFT STUDIES

The 96 samples of soil as prepared were used to study the potential drift of the quinhydrone electrode over a period of 15 minutes. Each determination was made in triplicate, and the last two were averaged and reported. Determinations were made at four soil-water ratios 1–1, 1–2.5, 1–10, and 1–100. As

TABLE 1

*pH Values of soils treated with various bases*

At indicated time intervals after addition of quinhydrone; averages for six soils, soil-water ratio of 1–1

| BASE SOIL WAS TREATED WITH | MOIST SOILS | | | | | | DRY SOILS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time intervals in minutes | | | | | | Time intervals in minutes | | | | | |
| | ½ | 1 | 2 | 5 | 10 | 15 | ½ | 1 | 2 | 5 | 10 | 15 |
| Na | 6.87 | 6.88 | 6.89 | 6.88 | 6.88 | 6.89 | 6.50 | 6.48 | 6.45 | 6.42 | 6.40 | 6.41 |
| K | 6.80 | 6.80 | 6.79 | 6.75 | 6.74 | 6.73 | 6.46 | 6.47 | 6.48 | 6.49 | 6.49 | 6.50 |
| Ca | 6.39 | 6.43 | 6.44 | 6.46 | 6.48 | 6.47 | 6.31 | 6.31 | 6.30 | 6.30 | 6.30 | 6.30 |
| Mg | 6.34 | 6.33 | 6.34 | 6.32 | 6.27 | 6.24 | 6.11 | 6.12 | 6.13 | 6.17 | 6.17 | 6.19 |
| $NH_4$ | 5.72 | 5.75 | 5.75 | 5.75 | 5.75 | 5.75 | 5.44 | 5.42 | 5.41 | 5.38 | 5.37 | 5.36 |
| Al | 4.42 | 4.40 | 4.36 | 4.33 | 4.32 | 4.30 | 4.25 | 4.18 | 4.17 | 4.17 | 4.14 | 4.14 |
| Fe | 3.59 | 3.58 | 3.53 | 3.46 | 3.44 | 3.42 | 3.16 | 3.14 | 3.13 | 3.12 | 3.10 | 3.08 |
| H | 3.71 | 3.70 | 3.69 | 3.67 | 3.66 | 3.65 | 3.25 | 3.24 | 3.23 | 3.21 | 3.17 | 3.17 |

TABLE 2

*pH Values of soils treated with various bases*

At indicated time intervals after addition of quinhydrone; averages for six soils, soil-water ratio of 1–2.5

| BASE SOIL WAS TREATED WITH | MOIST SOILS | | | | | | DRY SOILS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time intervals in minutes | | | | | | Time intervals in minutes | | | | | |
| | ½ | 1 | 2 | 5 | 10 | 15 | ½ | 1 | 2 | 5 | 10 | 15 |
| Na | 7.11 | 7.13 | 7.14 | 7.15 | 7.15 | 7.15 | 6.89 | 6.86 | 6.86 | 6.89 | 6.87 | 6.87 |
| K | 6.92 | 6.91 | 6.90 | 6.86 | 6.82 | 6.78 | 6.67 | 6.67 | 6.67 | 6.67 | 6.67 | 6.66 |
| Ca | 6.64 | 6.63 | 6.61 | 6.57 | 6.61 | 6.57 | 6.39 | 6.39 | 6.39 | 6.38 | 6.37 | 6.36 |
| Mg | 6.20 | 6.19 | 6.19 | 6.17 | 6.11 | 6.08 | 6.37 | 6.39 | 6.39 | 6.39 | 6.36 | 6.35 |
| $NH_4$ | 5.92 | 5.89 | 5.87 | 5.85 | 5.84 | 5.79 | 5.70 | 5.65 | 5.65 | 5.64 | 5.60 | 5.56 |
| Al | 4.30 | 4.27 | 4.22 | 4.19 | 4.14 | 4.10 | 4.16 | 4.12 | 4.12 | 4.12 | 4.11 | 4.08 |
| Fe | 3.93 | 3.92 | 3.76 | 3.68 | 3.63 | 3.57 | 3.39 | 3.37 | 3.37 | 3.32 | 3.27 | 3.24 |
| H | 3.76 | 3.74 | 3.71 | 3.66 | 3.62 | 3.59 | 3.36 | 3.36 | 3.34 | 3.30 | 3.25 | 3.20 |

all the six soils used gave similar curves the results have been averaged and reported in tables 1, 2, 3, and 4 for the various ratios. Thus each figure in these tables is an average of 12 determinations. In adding the water to the soil the weight of the air-dry soil was taken on the basis of the soil weight for the soil-water ratio.

From a study of tables 1 and 2 where the results of the studies of the soil-water ratios of 1–1 and 1–2.5 are reported, the ratios of lesser dilution and those most commonly used, it is not evident that pH drift is associated with any particular base at these dilutions; the greatest fluctuation between the ½-minute and 1-minute pH readings is 0.07 units in the case of the dried aluminum soil.

TABLE 3

*pH Values of soils treated with various bases*

At indicated time intervals after addition of quinhydrone; averages for six soils, soil-water ratio of 1–10

| BASE SOIL WAS TREATED WITH | MOIST SOILS | | | | | | DRY SOILS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time intervals in minutes | | | | | | Time intervals in minutes | | | | | |
| | ½ | 1 | 2 | 5 | 10 | 15 | ½ | 1 | 2 | 5 | 10 | 15 |
| Na | 7.38 | 7.35 | 7.32 | 7.30 | 7.26 | 7.24 | 7.37 | 7.31 | 7.30 | 7.25 | 7.22 | 7.14 |
| K | 7.21 | 7.14 | 7.08 | 6.98 | 6.91 | 6.81 | 6.81 | 6.78 | 6.77 | 6.76 | 6.70 | 6.67 |
| Ca | 6.73 | 6.72 | 6.61 | 6.57 | 6.49 | 6.45 | 6.53 | 6.52 | 6.51 | 6.49 | 6.47 | 6.45 |
| Mg | 6.19 | 6.16 | 6.10 | 6.01 | 5.96 | 5.91 | 6.57 | 6.53 | 6.50 | 6.47 | 6.43 | 6.41 |
| $NH_4$ | 5.93 | 5.87 | 5.79 | 5.76 | 5.70 | 5.64 | 6.10 | 6.08 | 6.03 | 5.96 | 5.86 | 5.81 |
| Al | 4.20 | 4.17 | 4.14 | 4.12 | 4.09 | 4.07 | 4.17 | 4.12 | 4.10 | 4.09 | 4.07 | 4.06 |
| Fe | 4.07 | 4.03 | 3.95 | 3.85 | 3.73 | 3.67 | 3.62 | 3.59 | 3.57 | 3.51 | 3.47 | 3.43 |
| H | 3.89 | 3.85 | 3.78 | 3.71 | 3.67 | 3.64 | 3.49 | 3.45 | 3.42 | 3.34 | 3.26 | 3.22 |

TABLE 4

*pH Values of soils treated with various bases*

At indicated time intervals after addition of quinhydrone; averages for six soils, soil-water ratio of 1–100

| BASE SOIL WAS TREATED WITH | MOIST SOILS | | | | | | DRY SOILS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Time intervals in minutes | | | | | | Time intervals in minutes | | | | | |
| | ½ | 1 | 2 | 5 | 10 | 15 | ½ | 1 | 2 | 5 | 10 | 15 |
| Na | 7.28 | 7.18 | 7.14 | 7.04 | 6.96 | 6.88 | 7.47 | 7.37 | 7.20 | 7.05 | 6.87 | 6.77 |
| K | 6.83 | 6.71 | 6.66 | 6.44 | 6.29 | 6.16 | 6.59 | 6.53 | 6.48 | 6.39 | 6.32 | 6.28 |
| Ca | 6.14 | 6.03 | 5.99 | 5.93 | 5.87 | 5.83 | 6.59 | 6.58 | 6.57 | 6.53 | 6.47 | 6.44 |
| Mg | 5.74 | 5.70 | 5.63 | 5.57 | 5.50 | 5.49 | 6.57 | 6.56 | 6.49 | 6.45 | 6.39 | 6.35 |
| $NH_4$ | 6.02 | 5.87 | 5.76 | 5.65 | 5.56 | 5.52 | 6.43 | 6.38 | 6.31 | 6.14 | 5.96 | 5.87 |
| Al | 4.37 | 4.32 | 4.28 | 4.26 | 4.22 | 4.21 | 4.63 | 4.54 | 4.50 | 4.46 | 4.43 | 4.41 |
| Fe | 4.41 | 4.32 | 4.21 | 4.09 | 4.02 | 3.97 | 4.07 | 4.02 | 3.93 | 3.87 | 3.81 | 3.79 |
| H | 4.21 | 4.15 | 4.08 | 3.96 | 3.91 | 3.89 | 4.10 | 3.95 | 3.84 | 3.71 | 3.65 | 3.61 |

This is hardly a significant figure in soil work. The greatest drift for the 1–1, and 1–2.5 dilutions over the 15-minute period is 0.36 units in the case of iron. This would be considered significant if it were not for the fact that at the greater dilutions both sodium and potassium show greater fluctuations than does the iron. The figures published by the International Society of Soil Science (4)

show that for several soils at the 1–2.5 dilution there is a pH drift of approximately 0.3 units from the ½-minute reading to the 1-minute reading. No drift of potential on the soils that we have studied even approximates this value.

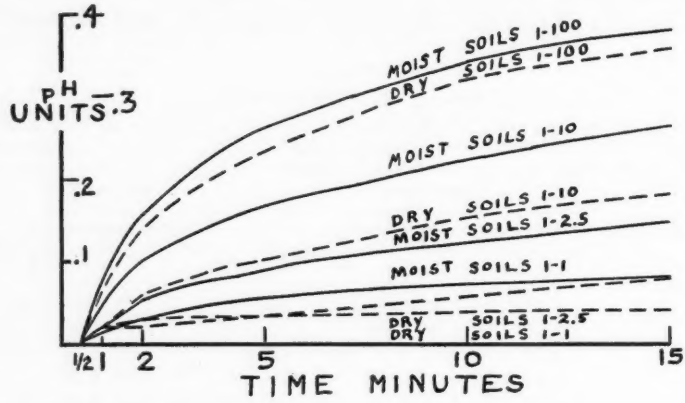


FIG. 1. DRIFT OF pH AT VARIOUS SOIL-WATER RATIOS
pH Units plotted against time

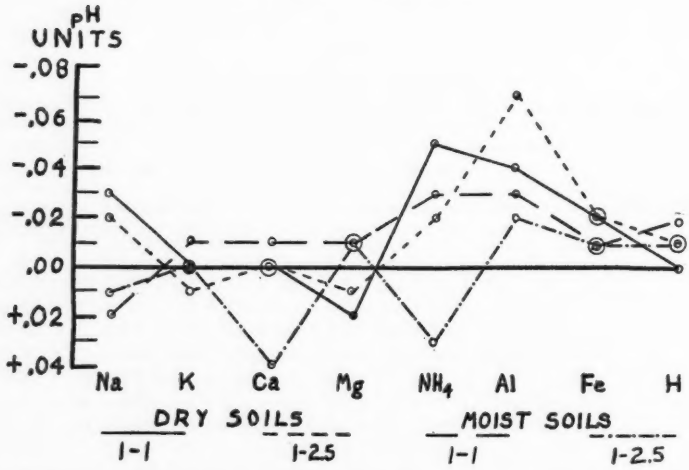


FIG. 2. DRIFT OF pH ONE-HALF MINUTE TO ONE MINUTE. SOILS TREATED WITH VARIOUS BASES. SOIL-WATER RATIO 1–2.5 AND 1–1

It is interesting to note that there is greater drift of pH in the case of soils that were saturated with water at the start than in the case of the dried soils. This is especially true for the drift at 2-minute and longer intervals. A study

of the tables will show the general trend of the drift for the dry soils as compared to the moist soils. The drift is emphasized by the curves in figure 1, which are drawn from the averages of each of the six soils treated with the eight bases. Thus each point in the curve shows the average drift of 48 samples. By averaging the results certain irregularities were smoothed over.

It should also be noted that the greater the degree of dilution the greater is the drift of pH value. This might be attributed to several things, among which is that in the more dilute soil suspensions there is less soil to act as a buffer against possible change in reaction.

It should also be noted that in some cases the drift of pH was observed over 18-hour periods. The figures obtained from these studies indicate that the curves are asymptotic and that the relative drifts shown at the 15-minute intervals are comparable to those obtained at the larger interval.

Curves drawn from the data herein presented showing the effect of dilution on pH value of the soils do not agree with the curves given by Perkins and King (12) for air-dry soils. However, it should be noted that there is good agreement between curves for the air-dried soils and the soils dried over calcium chloride. Discrepancies appear when one tries to match the curves for the moist soils with the curves for the dried soils.

## CONCLUSIONS

At the commonly used soil-water ratios exchangeable base has no influence on potential drift (fig. 2).

The amount of water contained by the soil apparently influences the degree of pH drift, the moist soils having a larger drift than the dry soils (fig. 1). This is especially true for the 2-minute period and longer periods of time.

The drift of pH is variable with degree of dilution, the greater the dilution the greater the drift (fig. 1).

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# FURTHER OBSERVATIONS UPON THE NATURE OF CAPILLARY RISE THROUGH SOILS[1]

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Received for publication April 27, 1931

In a previous paper (10) the writer and Alfred Smith[3] reported that a greater and more rapid rise of water by capillary movement from a free water table might be expected when soil columns of a relatively large cross section were used as compared to columns of smaller size. No explanation of this observation was made at that time. Continued interest has resulted in further studies, undertaken partly in Stanford University and more lately under the authority of the Hawaii Agricultural Experiment Station. Although the reasons for the results reported in the previous paper are still subject to some speculation, the investigations have led to a better understanding of the nature of capillary rise through soil.

Except as noted, the observations reported deal entirely with the movement of liquids in soils or other materials when those materials are supported over a free surface of that liquid. The reported rise of water is always vertical.

## EXPERIMENTAL

### *Observations with glass tubes*

Although it is recognized that the minute, branching and circuitous capillary conduits in a soil mass differ widely from those in an idealized arrangement of spherical grains, a study of such material is often illuminating. Meinzer (8) discusses the nature of the pore space in such idealized packings and points out that the pore spaces through such a system are capillary tubes of essentially triangular cross section. As the pore space follows the surface of the grains it enlarges in area and then diminishes to its former value as critical elevations are reached. Since in any random packing of sand grains perfect arrangement cannot be obtained, it may be assumed that the effective pore space, in a significantly large cross section, is essentially continuous and of practically uniform dimensions.

Consequently, studies were made of the rate of rise of water in minute glass tubes when erected over water. These capillary tubes were drawn from care-

[1] Published with the permission of the director.

[2] Associate professor of irrigation practice, University of Hawaii, and soil physicist in the experiment station.

[3] Associate soil technologist, California Agricultural Experiment Station.

fully cleaned glass tubes after heating in an oxygen flame. A heated section of less than 2 inches was quickly drawn to more than 4 feet. Short sections from the middle of this extended section were preserved for observation. From the method involved, it is evident that the minute tubes could not be perfect cylinders but necessarily are of varying radii. This effect, however, was not apparent in the observations. After each run the tube was reversed and a rise noted in the opposite direction. In no case did this reversal materially affect the characteristics of the rise. Precise observations of the rise of water through such systems are difficult. Although the probable error of a single observation of rise against time must be high, results for all tubes are consistent. Figure 1 illustrates the relation between observed capillary rise and elapsed time in a typical tube.

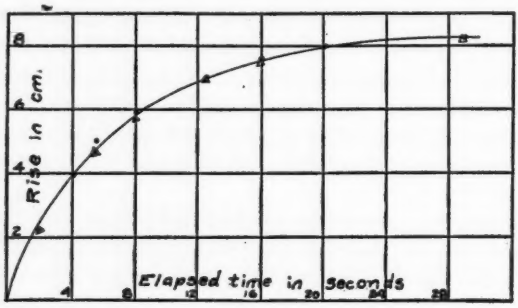


FIG. 1. RISE-TIME CURVE FOR GLASS TUBE OVER WATER

The shape of this curve (fig. 1), as well as the nature of the phenomena represented, indicates a curve of exponential form. Inspection and trial suggests the form:

$$R = K\,(1 - \epsilon^{-ct}) \qquad (A)$$

where $R$ = rise in centimeters after $t$ seconds, $\epsilon$ = the base of natural logarithms while $K$ and $c$ are constants, the first being the asymptotic value of $R$, while $c$ is probably a function of the diameter of the tube as well as the characteristics of the liquid used.

For the tube used in figure 1, the constants, as a close approximation, are

$$R = 8.25\,(1 - \epsilon^{-0.146t}) \qquad (B)$$

The closeness of the fit of equation $(B)$ to the observed points is also indicated in figure 1, observed points being shown as solid dots, while computed points are enclosed in triangles.

The difficulty of obtaining an unquestioned evaluation of the friction loss due to turbulence during the early rise, prohibits the setting up of a differential

equation covering the relation between rise and elapsed time. Equation (*A*) can only be considered as an empirical approximation.

*Observations with inert sands*

Meinzer's (8) description of the nature of the capillary conduits in clean spherically grained material would indicate that the capillary rise of moisture through such material should follow some such law as that suggested in equation (*A*). Ottawa testing sand was used to test this assumption. This material is commercially available in only two classifications; one of these is the 20–30 grade, all the material passing a standard 20-mesh screen and being retained on the 30-mesh, and the other is unscreened. The grains are not perfectly spherical, as seen through the microscope, but nearly so. Although essentially clean, the material was washed in 10 changes of water with constant agitation. The last washing was with distilled water.

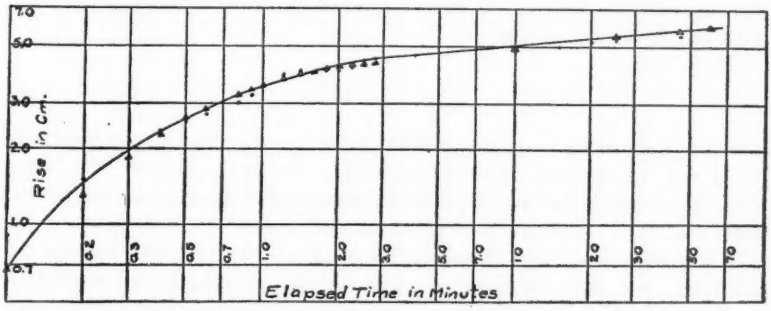


FIG. 2. LOG.-RISE LOG.-TIME FOR UNSCREENED TESTING SAND

Since a limited assortment of screens was available, only three separates from the unscreened material were possible. The screened separates were 20–35, 35–48, and 48–65. The mill screened, 20–30, separate added another lot. The washed, unscreened sand was also used.

These sands were carefully packed into 2-inch glass tubes fitted with brass screens at the lower end. Practically constant volume weight was obtained throughout each tube by the method already described (10). At least 10 columns of each material were used.

These columns were erected over distilled water, zero-hour being the time at which water in the sand mass had attained the elevation of the water in the reservoir. Elapsed time was taken with a stop watch. Frequent observations were made, especially at the beginning of each run, the time interval between observations during this period being one-tenth of a minute. This interval increased as the rate of rise was reduced. All sand columns were under observation for 60 minutes.

In general, the curves resulting from plotting log-rise against log-time showed the same general form. This form is illustrated in figure 2, which represents the observations taken on run 6 of the unscreened material plotted logarithmically. Here the initial arm of the curve is similar in form to the exponential curve noted for the glass tube. The curve does not reach an asymptotic value as might be expected, however, the second phase of the rise being parabolic for the period between 2.8 to 60 minutes. The parabolic nature of the upper part of the curve has already been noted, when soils are used, by McLaughlin (6) who derives empirical equations for rise against time in this phase of his observations. In the results reported in the previous paper (10) the parabolic nature of the curves continued for about 150 days. In general, the initial phase of the curve has not been studied.

Although there is no mathematical discontinuity in such curves as that illustrated in figure 2, there seems to be some evidence that two processes, acting simultaneously, are effective. One of these is of primary significance during the initial phase of the rise, whereas the other is evidenced by the long, slow rise in the second arm.

The equation

$$R = K\,(1 - \epsilon^{-ct})t^n \qquad (C)$$

where $n$ = a constant and equals the slope of the straight arm, other symbols being as given, seems to fit these conditions. For small values of $t$ the factor $(1-\epsilon^{-ct})$ dominates the rate; for large values of $t$ the binomial becomes practically unity and the equation of the parabola remains.

When proper values are chosen for the constants, the computed rises for the given time periods fit the observed points with acceptable accuracy when clean sands are used, in view of the approximation mentioned for equation (A). Great precision of observation cannot be expected during the early readings when the rise is rapid and the interval short. Moreover, errors are seemingly exaggerated in this region because of the nature of the ruling used.

Suitable values of the constants for the curve in figure 2 give an equation:

$$R = 3.85\,(1 - \epsilon^{-2.58t})t^{0.108} \qquad (D)$$

In this determination, and all that follow, $n$ is the natural tangent of the slope of the second arm, $K$ is the intercept of the second arm extrapolated to unit time, and $c$ is the average value obtained by considering each of the observed points in turn, in view of conditions already established. Computed values for rise from equation (*6*) are shown in triangles in figure 2. Although the fit is far from perfect, it may be considered as a first approximation. It should be noted that the first observation, after 6 seconds of run, usually shows a greater rise than the computed value.

Equations for all other runs were determined in the same way. These equations may be summarized by listing the average value and probable error of each of the constants involved.

The results of these computations are given in the following:

| *Separate* | *Equation* | |
|---|---|---|
| 20–30 | $R = 0.97 \pm 0.07\ (1 - \epsilon^{-(6.18 \pm 0.34)t})\ t^{0.113 \pm 0.013}$ | (*E*) |
| 20–35 | $R = 2.30 \pm 0.06\ (1 - \epsilon^{-(3.54 \pm 0.11)t})\ t^{0.069 \pm 0.005}$ | (*F*) |
| 35–48 | $R = 2.40 \pm 0.05\ (1 - \epsilon^{-(3.16 \pm 0.204)t})\ t^{0.061 \pm 0.005}$ | (*G*) |
| 48–65 | $R = 4.41 \pm 0.09\ (1 - \epsilon^{-(2.07 \pm 0.05)t})\ t^{0.129 \pm 0.004}$ | (*H*) |
| Unscreened | $R = 3.41 \pm 0.11\ (1 - \epsilon^{-(2.53 \pm 0.17)t})\ t^{0.131 \pm 0.006}$ | (*I*) |

In general, the value of the coefficient increases with decreasing grain sizes, while the value of the constant factor in the exponent decreases in the same sense. Although the points as plotted in figure 3 show general trends as indicated in the foregoing, they depart widely from simple relationships. The

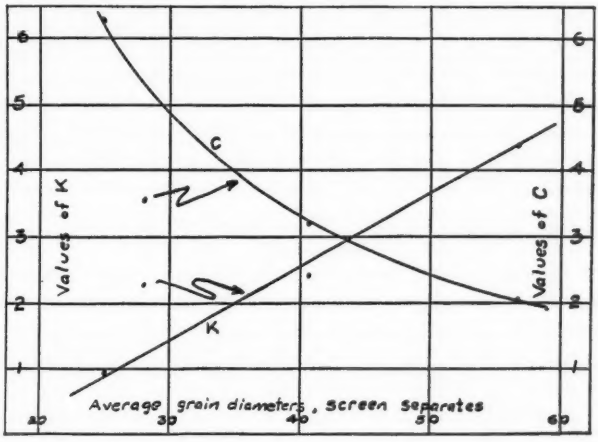


FIG. 3. RELATION BETWEEN CONSTANTS FOR TESTING SAND AND GRAIN-SIZES INVOLVED

lines drawn on figure 3 illustrate trends only and have little quantitative significance. Departures from simple trends are most pronounced in the largest hand-screened separates. Here the values for both constants indicate an average size much smaller than the average screen-size used in its separation. No information is available with respect to the distribution of grain sizes between the specified limits. If the normal unscreened material had been robbed of a large part of its 20–30 separate before shipment, the 20–35 separate as prepared in the laboratory would be rich in the finer sizes, and some such result as noted might be obtained.

Another significant conclusion from the equations for rise against time with inert materials is that the exponent of $t$ is apparently independent of the grain size. Although these values range from $0.061 \pm 0.005$ to $0.131 \pm 0.006$, there is no consistent relation with grain size. Here the arithmetic

difference is about nine times its probable error. Although such a ratio is ordinarily enough to establish significance in a difference, the relatively large probable error attached to each term and the similarity of values at each end of the grain-size series seem to reduce the significance in this case.

However, this value seems somewhat dependent upon the physical conditions of the liquid, as may be noted when soils of such texture are used, that the second arm may extend for several days before ceasing to follow the parabolic law. When such a column is subjected to extreme diurnal changes of temperature, the first observation in the morning is consistently above its extrap-

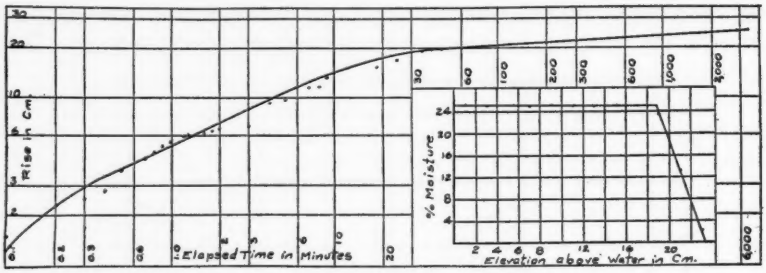


FIG. 4. LOG.-TIME LOG.-RISE FOR FINE EMERY, TOGETHER WITH RESULTING MOISTURE DISTRIBUTION

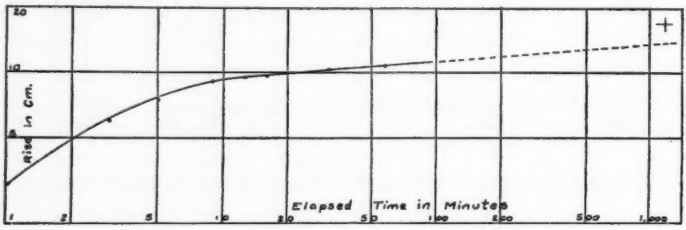


FIG. 5. LOG.-RISE LOG.-TIME CURVE FOR UNWASHED BUILDING SAND

olated position as determined by observations on the previous day. Although both surface tension and viscosity increase with lowered temperature, the effect of surface tension in this case seems more marked. This effect is illustrated by the last point in figure 5.

*Observations with finely ground emery*

The possibility of noting a change in the nature of moisture distribution at or near the point at which the rise began its distinctly parabolic aspect, led to the substitution of finely divided emery for sand. In commercial lots this material is described by the screen number of the smallest screen that will

allow all the grains to pass. No measure of the smallest grain is available, nor is the distribution of sizes known. Moreover, the grains are distinctly angular. Commercial emery is apparently coated with a thin film of oil. This material was removed by ether extraction by means of an Allihn condenser and a final flushing with clean ether.

This washed and dried material was packed into a 2-inch glass tube formed by cementing together the ground faces of glass sections, each 2 cm. high, with a thin layer of rubber cement. The assembled tube was reenforced by a wooden trough into which the tube was lashed. McLaughlin (7) reports a similar arrangement. With the brass sections used by McLaughlin, observations of rate of rise were impossible.

Observations of rise against time were made as usual, the results being presented in figure 4. Here the nature of the initial phase is distinctly different from the characteristic exponential form of the more uniform sand. In fact, a straight line might represent the observed points as well, or better, than the arbitrary curve in figure 4. Considerable difficulty was experienced with this material because little or no color change was apparent upon wetting. In fact, no rise above 20 cm. was evident through the glass, although upon disassembling, distinctly wet emery was encountered at 25 cm. In this case the straight arm is drawn by analogy. It is assumed that the rise was real, although not apparent through the glass, between 40 and 2,400 minutes, and that it followed the parabolic law during this period. The column was disassembled after 2,400 minutes. Each section was removed with a broad spatula and placed at once in a weighing bottle. Drying was accomplished as usual, at 110°C. The resulting moisture distribution is also shown in figure 4. Here all samples below 19 cm. showed essentially uniform moisture contents at the percentage subsequently identified as the saturation percentage. Greater elevations were characterized by continuously decreasing moisture contents.

### *Observations with soils*

When soils are used the rather distinct and easily defined conditions described in the foregoing become much more complex. The size of grain involved and the distribution of grain sizes is no longer known with any exactness, whereas colloidal material may affect the results in many ways. Moreover, soluble material undoubtedly affects both surface tension and viscosity. Consequently, curves of rise against time are inconclusive and of difficult interpretation.

However, some of the characteristics of the curves from simple materials remain. They are all characterized by the parabolic arm in the second phase of the rise, and in general the slopes of these lines when plotted logarithmically are essentially the same. The time required for the inauguration of the parabolic arm is often very long, especially with fine-grained material. Moreover, all such parabolic curves eventually cease their simple relations and approach an asymptotic value. In general, the finer grained the material the more extended is the parabolic part of the curve.

When soils are used the initial curve described for sands as one of exponential character tends to approach the parabolic form suggested by the initial curve for emery. The general form suggested in equation (*C*) no longer holds, since the coefficient of the exponent $t$ becomes a variable. In fact, with many soils the initial arm is practically straight for a considerable time, and then through a long curve assumes the characteristic parabola of the upper arm.

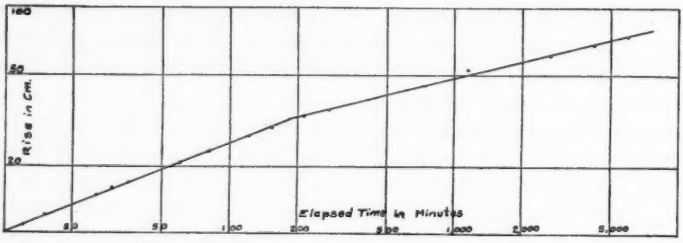


FIG. 6. LOG.-RISE LOG.-TIME FOR YOLO SANDY LOAM

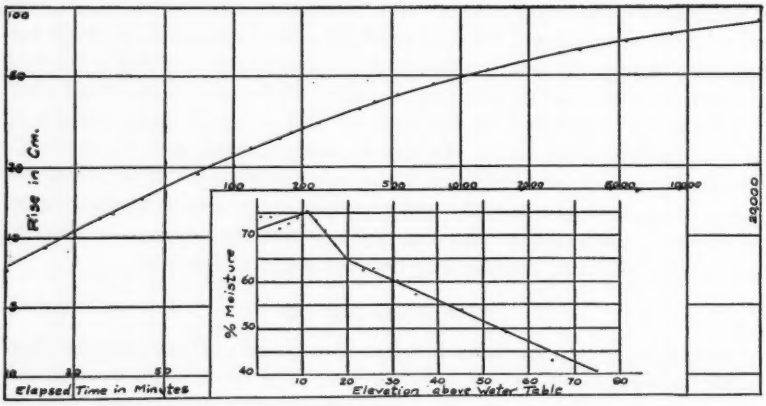


FIG. 7. LOG.-RISE LOG.-TIME CURVE FOR NATURAL KUNIA SOIL, TOGETHER WITH RESULTING MOISTURE DISTRIBUTION

The fineness of soil grain involved seems to be the dominating influence in determining the length of this initial arm of the curve. When ordinary building sand was used, the parabolic section of the curve began at about 15 minutes. With Yolo fine sandy loam, less than one day was required, whereas with a fine-grained soil from the pineapple fields at Kunia (Oahu, Hawaii), no sign of parabolic rise was evidenced for four days. Similar soil, exposed to a temperature of 1,100°C. for about five hours was so finely divided that the top of the 100 cm. tube was reached in 1,500 minutes without any evidence of the characteristic change of rate which might be expected.

Details of the log-rise, log-time relations are shown in figures 5, 6, 7, and 8.

Apparently, the sample conception of an exponential curve giving place to a parabola fails when angular, fine-grained materials are used. There seems to be some evidence that the curve representing the initial arm flattens out approaching a parabola, whereas the second arm, which is perhaps entirely parabolic with spherical material, becomes parabolic with soils only after an appreciable time. Since the curve leading to this parabola is tangent to the modified exponential of the initial phase, all evidence of a discontinuity, such as is noted with sand, disappears. The curves in figures 7 and 8 show no evidence of such discontinuity. However, from soil moisture sampling it is

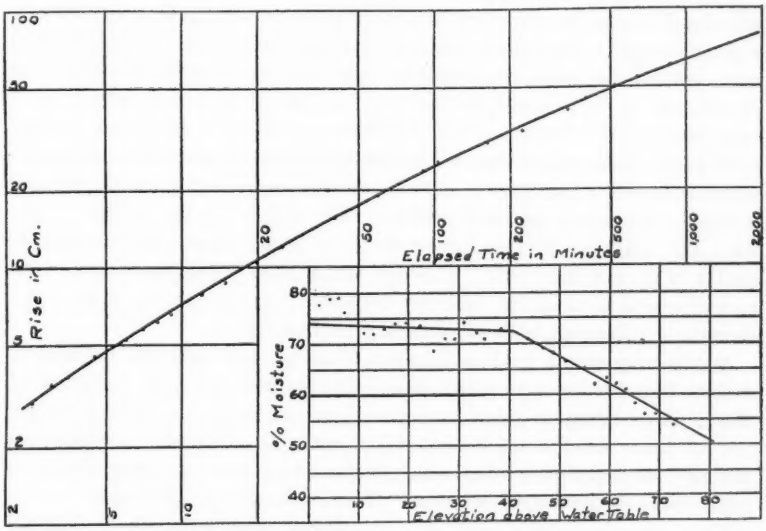


FIG. 8. LOG.-RISE LOG.-TIME CURVE FOR HEATED KUNIA SOIL, TOGETHER WITH RESULTING MOISTURE DISTRIBUTION

evident that some change in the process of rise is introduced at 20 cm. in figure 7 with normal Kunia soil, and at 40 cm. in figure 8. It is assumed that these points mark the ends of the modified exponential rise and the beginnings of the modified parabolic rise. The significance of these points is masked in the log-time, log-rise curves by the continuity of the curves passing through them.

### *The distribution of soil moisture in capillary columns*

McLaughlin's (7) observation that the distribution of moisture in capillary soil systems is characterized by a zone of high moisture content which extends for some distance above the water table and then by consistently and uniformly

decreasing moisture contents seems to support the assumption of discontinuity of rise proposed above. All efforts to correlate the position of this discontinuity in moisture distribution with the elevation at which exponential rise gives place to parabolic rise with sands, failed because of the difficulty of obtaining a sufficient number of samples from the short column available.

The relation between rates of rise and moisture distribution with emery has already been mentioned and is illustrated in figure 4. Here the column is saturated to an elevation of 19 cm., the rest of the rise being marked by continuously and uniformly decreasing moisture contents. The same elevation marks the beginning of the parabolic aspect of the rise-time curve.

Moisture distribution in the true soils is not so simple. When normal kunia soil (fig. 7) is used, a zone of maximum moisture content, is found at 10 cm., a zone of rapidly decreasing moisture continues to 20 cm., beyond which a more gradual but very consistent decrease continues to 55 cm. Moisture distribution in the heated Kuniz soil (fig. 8) shows no zone of maximum moisture content but a stratum of high moisture content to 40 cm., beyond which fairly uniform decrease occurs. The significant point about such distribution seems to be that a large part of the column is characterized by a uniformly and gradually decreasing moisture content. This section of the column begins when the eratic distribution during the initial phase ceases and continues to the top of the wetted section. Although McLaughlin (7) emphasizes the presence of a zone of maximum moisture content, often encountered in the lower elevations, this seems to be of secondary importance.

Another significant relation between elevation and moisture content is evident from studies with a relatively coarse-grained soil from the Island of Maui. After being air-dried, stored, and screened through a 48-mesh screen, this soil has a moisture equivalent of 28.0 per cent. This mixed material was packed in sectional glass tubes, which permitted intensive sampling within the upper zones of the wetted columns. Three columns were prepared.

The columns were disassembled in the manner already described, when the moisture had reached 66 cm. in one case, 87 cm. in another, and 120 cm., for the third. These elevations may be called $W$. The fact that the last column had practically reached its ultimate rise was evidenced by the log-time, log-rise curve, which had begun to depart from its parabolic shape and assume an asymptotic value. Moreover, the line of demarkation between wet soil and dry soil became increasingly indistinct at about 114 cm. This characteristic has often been noted as the rise approaches its maximum.

In each case three samples were taken above the significantly wetted column, and enough samples were taken from below this line of demarkation to identify the characteristics of the moisture content-elevation curve. All samples came from the section above the region characterized by a constant slope in the log-time, log-rise curve. When moisture contents below $W$, in each case, were plotted against elevations, a straight line resulted, whereas moisture contents above $W$, similarly plotted, fell off rapidly, reaching the air-

dry moisture content in less than 6 cm. In the third case, that in which the rising moisture was allowed to approach its maximum elevation, the discontinuity in the moisture content-elevation curve was not so sharply marked as in the two other cases. The point of change, however, was easily noted at 114 cm. of elevation, which has been reported as the point at which the sharp distinction between the wetted soil and dry soil became less pronounced.

The moisture contents at the elevations of discontinuity in moisture distribution were surprisingly similar, being 32.6 per cent for the 67-cm. column, 32.0 per cent for the 87-cm. column, and 32.0 per cent for the 120-cm. column. The similarity of these values seems significant since they all closely approximate the maximum water-holding capacity for the soil in question. Experience with many Hawaiian soils indicates that the moisture equivalent multiplied by 1.1 gives a fair approximation of the field capacity. The field capacity for the soil used computed in this base was 30.8 per cent. Since the

TABLE 1

*Summary of the relation between moisture equivalent and the moisture content at the top of capillary columns*

Reported by McLaughlin

| SOIL TYPE | NUMBER OF COLUMNS | MOISTURE EQUIPMENT | AVERAGE MOISTURE AT TOP OF WETTED COLUMN |
|---|---|---|---|
| | | *per cent* | *per cent* |
| Idaho sandy soil | 4 | 4.7 | 5.5 |
| Riverside soil | 1 | 7.9 | 9.8 |
| Idaho Lava Ash soil | 3 | 18.3 | 18.8 |
| Santa Clara soil | 3 | 20.8 | 22.6 |
| Whittier soil | 1 | 38.3 | 34.8 |
| Utah soil | 1 | 22.2 | 20.4 |

samples came from a 2-cm. section of increasing moisture content, it is evident that the moisture content at the precise top of the wetted section would be somewhat less than that reported.

Moreover, it seems clear that the slope of the moisture-content, elevation curve becomes less as the wetted column increases in length. Apparently this slope decreases to a given value which may be a characteristic of the soil used. Rise by the action of surface forces apparently ceases when this asymptotic slope or "capillary gradient" is reached. The slopes for the three columns listed in the foregoing were 0.293, 0.164, and 0.073 respectively. It is interesting to note that the points obtained by plotting the values of $W$ against the resulting capillary gradient are themselves essentially collinear.

McLaughlin's (7) work on the moisture distribution in capillary tubes shows a similar relation between moisture equivalent and the moisture content at the top of the wetted column, although his results have never been presented

from this point of view. McLaughlin reports studies on six soils with moisture equivalents ranging from 4.7 per cent for an Idaho sandy soil to 38.2 per cent for a Whittier (California) soil. Although the consistent decrease in moisture content in the upper part of his columns is apparent, the termination of this series at the upper end is not so clearly defined as those reported, because in some cases maximum rise had been attained. However, the moisture content at this point can be closely approximated. A summary of results, obtained from an analysis of McLaughlin's work, is presented in table 1.

A typical curve from McLaughlin's work is shown in figure 9. Distribution of moisture in this column is characterized by a zone of maximum moisture content extending to about 8 inches and by uniformly decreasing moisture contents from 8 inches to 20 inches. McLaughlin's zone of maximum moisture contents does not seem to be present in this particular column.

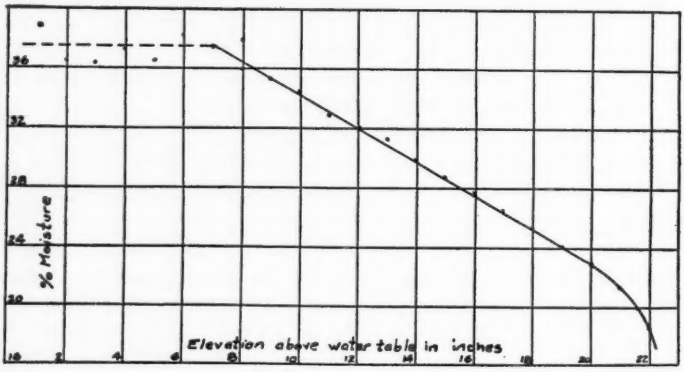


FIG. 9. MOISTURE DISTRIBUTION CURVE FOR SANTA CLARA SOIL (AFTER MCLAUGHLIN)

*The effect of the size of container*

When the results of observations described in the previous paper (10) are viewed in the light of a modified form of equation (3), the significance of the difference between the performance of large columns and small columns becomes less marked. As has been indicated, the parabolic arm of the rise is common to all such curves, the slopes of these lines, in general, being similar. With soils, however, the second factor of equation (*c*) $1 - \epsilon^{-ct}$, changes form and has not been determined. This factor apparently influences the time elapsing between zero-hour and the time at which the parabolic rise becomes marked. If so, it may be eliminated from a consideration of the ultimate performance of the column. If this is done

$$R = Kt^n \qquad (J)$$

adequately expresses the relation of $R$ and $t$, with the provision that $t$ must be relatively large. Table 2 gives the values of $n$ and $K$ for the various column sizes reported, the ratios of perimeter to area, and the elevations of the zones of maximum moisture content for each of the sizes previously reported.

The values of $K$ for each of the sizes are essentially the same, whereas $n$, the other variable, increases with apparent significance in only the two smallest columns. Columns of the 3-inch, 4-inch, and 5-inch size seem to show increasing ultimate rise because of fortuitous combinations of $K$ and $n$.

The cause of the small value of $n$ for the smaller sizes is not clear. The longer perimeter per unit cross section may be responsible. More compact packing is possible in internal areas than along the perimeter. If most of the rise takes place in internal elements of the column, it is clear that the rise must be at a slower rate in small columns than in large ones since with the small columns a significantly large part of the water lifted per unit time is lost later-

TABLE 2

*Constants for equation (J) together with elevation of zone of maximum moisture content for previously reported columns*

| ONE DIMENSION OF SQUARE COLUMN | $\frac{P}{A}$ | $K$ | $n$ | ELEVATION TO MAXIMUM WATER ZONE |
|---|---|---|---|---|
| *inches* | | | | *cm.* |
| 1 | 4.0 | 64.5 | 0.063 | 10 |
| 2 | 2.0 | 60.0 | 0.134 | 14 |
| 3 | 1.3 | 60.0 | 0.151 | 26 |
| 4 | 1.0 | 68.0 | 0.129 | 32 |
| 5 | 0.8 | 65.0 | 0.141 | 29 |
| 6 | 0.7 | 66.5 | 0.146 | 33 |
| 8 | 0.5 | 66.0 | 0.141 | 30.5 |
| 12 | 0.3 | 66.0 | 0.143 | 30.5 |

ally to increase the moisture content at the perimeter, less being available for vertical rise. When larger columns are considered, this effect decreases and apparently becomes insignificant with columns larger than 2 inches square. Subsequent observations with the same soil in cylindrical celluloid columns with diameters of 2 inches and 4 inches showed no difference in rate of rise.

The influence of perimeter is again noted in the position of the zone of maximum moisture content. Significant increases of elevation are noted as the size increases to 2 and possibly 3 inches. Further increase in size is not effective in increasing this elevation.

## DISCUSSION

Although much has been written with respect to the physics of capillary distribution from a free water table, the mechanics of the process is still far from clear. Briggs (2) and Buckingham (3) attribute the rise to differences

in the surface curvature of soil water masses lying between adjacent grains. The resulting upward tension is supposed to lift water from the reservoir at the bottom of the column, carry it through the connecting films, and use part of it at least in increasing the radius of curvature of the water surface immediately above the last wetted grain. Because of the ever increasing weight of supported water, the moisture masses between the grains decrease in volume and the enclosing films become thinner as elevation is gained, the moisture percentage supposedly decreasing in the same sense. Moisture presumably ceases to rise when the wedge-shaped masses become insignificantly small.

McLaughlin's (7) observation that such moisture distribution follows no such simple rule, but is characterized by a zone of maximum moisture content appreciably above the water table, has never been satisfactorily explained. Nor can these well-substantiated observations be justified by Briggs' (2) conception.

Keen (5) visualizes capillary rise through soils as being more analogous to the usual phenomena in a capillary tube, assuming, as has Meinzer (8), that the pore space in a soil may be compared to a bundle of capillary tubes of various diameters this variance depending upon the range and distribution of grain sizes involved.

From theoretical reasoning concerning moisture distribution, Keen concludes that we might expect to find three rather distinct moisture horizons in such a capillary system. The lowest of these should, according to Keen, be marked by complete saturation, the next by complete saturation of the smaller pores and incomplete saturation of the larger ones, and finally a region of incomplete and decreasing moisture. Keen's conclusions seem to be well supported by the moisture determinations reported in the foregoing if the region of relatively low moisture content, which is sometimes found immediately above the water table, be disregarded.

As has been indicated, the exponential form of the rise-time curve during the first phase of rise is observed with relatively coarse spherical sand grains as shown in figure 3. This relation is no longer evident when fine, angular materials such as emery or soils are used, although in such cases there is some suggestion of discontinuity in the entire curve. The cause for this change is not clear. Resistance to flow through the irregular capillaries of a mass consisting of irregular fragments probably increases rapidly as size-range and angularity increase. Consequently, the locus of points resulting from plotting rise against time for such materials would fall consistently below the exponential curve, approaching the parabolic form noted in figure 6. Some such form as

$$R = ct^m (1 - e^{lt}) \qquad (K)$$

might express the initial phase of rise if the ratio of $c$ to $l$ were considered as a function of the range of grain sizes and their angularity, this ratio being large with such material as inert sand and small for emery. No attempt has

been made to evaluate the constants suggested in equation ($K$). The colloidal material in the soil with its volume-increase upon wetting adds another factor which would necessarily enter equation ($K$) if used for other than inert materials. Consequently, equation ($K$) is of only speculative interest.

Bouyoucos (1) seems to believe that colloidal swelling with the consequent closure of capillary conduits is of dominating importance when soils are under observation. He reports that if columns of dry clay are placed over water and kerosene, the organic liquid at the end of three days will have risen four or five times as high as the water in spite of its lower surface tension, because of the inability of the colloidal material to absorb the kerosene and consequently reduce the effective pore space. Local results fail to substantiate this finding. A Waipio (Oahu) soil of high colloidal content exhibited less rise after 30,000 minutes when supported over kerosene than when supported over water. Moreover, the parabolic curves for the second phase were essentially parallel. Local soil colloids are lean in silica and rich in iron and alumina. These colloids have never been studied with respect to swelling. The low sesquioxide ratio of the Waipio colloid may be associated with a small capacity for volume increase.

Although the relation between moisture distribution and the transition to parabolic rise is marked with emery, the relation is poor with soils. In figure 7 observations upon rate of rise of moisture with an unheated Kunia soil show no parabolic relation between rise and elapsed time until an elevation of 65 cm. has been reached. Moisture determinations, however, indicate a uniformly decreasing moisture content beginning at 20 cm. The possibility of this being due to colloidal activity and a throttling action, brought about in some way by colloidal volume-increase, is discounted by the fact that the same material when heated to 1100°C in an electric muffle, a temperature which according to Whitney (9) should inactivate the colloidal material, showed a similar relation but to a more marked degree. In figure 8 the parabolic relation between rise and elapsed time had not begun at 80 cm., although the discontinuity in moisture content was marked at about 40 cm.

Perhaps a better hypothesis than one involving the conception of swelling colloids, lies in assuming that the true parabolic nature of the second phase of rise is only apparent when soil grains are so large that turbulence with consequent energy loss at the beginning of this phase is negligible. For other materials the second phase, if it is assumed to begin at the point of moisture discontinuity, is characterized by a smooth curve tangent to that of the first phase and becoming parabolic after an elapse of time, which increases with the fineness of grain.

If this assumption is made, the discontinuity of moisture content should be taken as the point at which the rate of soil-moisture decrease with elevation, becomes essentially uniform to the top of the wetted section. This point would be marked by 20 cm. for figure 7, 40 cm. for figure 8, and 19 cm. for figure 4. Irregularities in moisture, lower than this point, as in figure 7 and

as emphasized by McLaughlin (7), probably depend upon a trapping of air in the lower horizons due to rapid rise through the more open passages in the case of increasing moisture, and to the successive failure of certain zones to attain saturation because of large pore spaces caused by varying grain sizes and random packing in the case of decreasing moisture.

As has been indicated, Briggs (2) assumes that capillary equilibrium is attained when the films of moisture surrounding soil grains and the water in the wedge-shaped masses lying between them are insignificant and the moisture content is consequently small. Although such may be the case with inert materials, the analysis of moisture distribution indicates that a soil may contain significant quantities of water under certain conditions and lose it only slowly, if at all, by true capillary movement. The quantitative relation of this water to the maximum water-holding capacity adds interest to Buoyoucos' (1) assumption that a large part of the water in a soil at the maximum field capacity is colloidally imbibed. Whitney (11) seems to hold the same view.

Furthermore, it seems clear from other studies that when a soil is wetted to a moisture content no greater than the maximum water-holding capacity, water is available for distribution to adjacent dry soil at an extremely slow rate. Veihmeyer (9) has demonstrated that dry soils packed in close contact with damp soils, wetted either artificially or by irrigation, have little capacity to increase in moisture content. The same principle, under field conditions, has been shown by many workers in modern studies of the effectiveness of a soil mulch. Conrad and Veihmeyer (4) demonstrate the same principle from a different point of view.

In field studies, in the absence of a free water table, the soil when in equilibrium with gravity is rarely at a higher moisture content than its field capacity. At this moisture content capillary movement, upon the principle outlined in the foregoing, is not a significant factor in moisture distribution. The necessary conclusion is that little or none of the moisture in a normal, well-drained soil is in the films and wedge-shaped masses surrounding the granules comprising the capillary system. If this water is colloidally imbibed, studies in the relation of plants to soil moisture assume a different aspect.

## SUMMARY

Some evidence is furnished that capillary rise of water through inert sands and through soils is a compound process dominated in the first phase by an action which may result in a complete filling of the pore spaces, and in the latter phase by an action which results in a continuous, uniform decrease in moisture content.

When coarse, inert materials are used, the transition between these two processes can be noted by inspection of the log. rise-log. time curve. With fine materials inspection of the moisture distribution is required.

The minimum moisture content reached by true capillary distribution in soils is about the maximum field capacity. Subsequent movement is at a very slow rate and must be attributed to other causes.

It seems clear that soil-moisture under normal field conditions cannot possess much motility since such moisture contents are rarely more than the maximum water-holding capacities of the soil in question.

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# EFFECT OF REPLACEABLE SODIUM ON SOIL PERMEABILITY[1]

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Experience has shown that a good soil contains a large amount of replaceable bases. Such a soil can function more efficiently as a pH regulator. The ultimate state of dispersion, however, depends not only upon the amount of the replaceable bases but upon their relation one to another. From a practical standpoint it is known that calcium in the exchange complex acts favorably upon the soil structure, whereas sodium has an opposite effect, leaving the soil sticky and impermeable.

The reclamation of alkali lands depends to a great extent upon soil permeability, determined largely by its degree of dispersion. In this study of the effect of replaceable sodium in various amounts on soil permeability, it was hoped to obtain a mathematical expression for permeability in terms of replaceable sodium or in terms of the ratio of sodium to the total replaceable bases. The value of such an expression is evident. It would enable the investigator to compare approximate speed of water penetration for different relative amounts of sodium saturation and thus be a satisfactory guide as to the type of reclamation to be pursued. When the relation between soil permeability and replaceable sodium is known it is also possible to calculate the time required to replace sodium by calcium in a calcareous soil by continuous leaching with irrigation water. The calculation given is theoretical in part although based largely upon the experimental relation between ($k$)[3] transmission constant and ($S$) ratio of replaceable sodium to total replaceable bases.

## EXPERIMENTAL

The experimental work was conducted on a heavy, calcareous, alkali soil of Cache Valley. The samples collected from the surface horizon varied widely

[1] Contributed from Utah Agricultural Experiment Station in coöperation with Division of Agricultural Engineering, U S. Bureau of Public Roads. The coöperative work is conducted under the immediate supervision of the following committee, each member of which has coördinate responsibility: D. S. Jennings, soils; Willard Gardner, physicist; and O. W. Israelsen, irrigation and drainage engineer. The chemical work was directed primarily by D. S. Jennings and the mathematical analysis of the problem, together with the percolation studies, by W. Gardner.

[2] Graduate student. Publication authorized by director, June 2, 1931.

[3] Rate of percolation expressed in C. G. S. units, e.g., $k = \frac{\text{cc.}}{\text{cm.}^2 \text{ sec. } 980}$.

*Note:* There is no pressure head, but a constant force of 980 dynes is acting on each gram.

TABLE 1

*Analyses of replaceable bases*

| LABORATORY NUMBER | DEPTH | $CO_2$ | DISSOLVED ANIONS* | | REPLACEABLE BASES, MILLIEQUIVALENT PER 100 GM. | | | | | | TOTAL BASES | $(NH_4)$ ABSORBED | RELATIVE PROPORTIONS | | | | $T \times 10^{+3}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Percentage | | Total | | Corrected | | | | | | Ca | Mg | Na | K | |
| | | | $SiO_2$ | $CO_2$ | Ca | Mg | Ca | Mg | Na | K | | | | | | | |
| | *inches* | *per cent* | | | | | | | | | | | | | | | |
| 1878 | 6 | 6.87 | 0.265 | 0.38 | 30.5 | 11.1 | 9.5 | 6.1 | 3.4 | 1.1 | 20.1 | 15.6 | 49.6 | 32.0 | 17.9 | 0.5 | 4.1 |
| 1879 | 15 | 17.8 | 0.036 | 0.42 | 23.0 | 11.0 | 7.0 | 7.0 | 2.7 | 1.1 | 17.8 | 13.8 | 39.2 | 39.2 | 15.2 | 6.4 | 4.5 |
| 1882 | 60 | 14.6 | 0.144 | 0.32 | 21.0 | 11.0 | 5.7 | 7.0 | 6.2 | 2.3 | 21.2 | 14.9 | 26.9 | 35.0 | 29.3 | 10.8 | 0.5 |
| 1872 | 4 | 0.34 | 0.203 | 0.125 | 18.4 | 8.5 | 8.5 | 6.0 | 2.7 | 0.04 | 17.2 | 14.3 | 49.4 | 34.8 | 15.7 | 0.1 | 6.2 |
| 1873 | 14 | 9.60 | 0.182 | 0.330 | 20.8 | 10.5 | 4.0 | 6.2 | 9.7 | 0.1 | 19.0 | 14.8 | 21.0 | 32.6 | 51.0 | 0.4 | 1.2 |
| 1876 | 50 | 18.1 | 0.077 | 0.250 | 12.7 | 9.2 | 1.7 | 6.4 | 7.3 | 0.44 | 15.9 | 11.7 | 10.7 | 40.2 | 45.9 | 3.2 | 1.3 |
| 1867 | 8 | 1.24 | 0.154 | 0.210 | 14.0 | 3.0 | 2.2 | 0.2 | 18.0 | 0.2 | 20.6 | 17.5 | 10.6 | 0.95 | 87.5 | 0.95 | 0.38 |
| 1868 | 18 | 14.2 | 0.075 | 0.410 | 16.1 | 8.5 | | 3.4 | 14.2 | 0.1 | 17.7 | 17.2 | | 19.2 | 80.1 | 0.7 | 0.80 |
| 1871 | 60 | 11.4 | 0.210 | 0.220 | 14.9 | 6.4 | 0.9 | 3.4 | 13.2 | 0.3 | 17.8 | 15.0 | 5.0 | 19.1 | 74.4 | 1.5 | 0.20 |
| 1884 | 8 | 2.76 | 0.101 | 0.260 | 15.5 | 7.1 | 3.4 | 4.1 | 10.4 | 0.7 | 18.6 | 17.4 | 18.3 | 22.0 | 56.0 | 3.7 | 0.94 |
| 1885 | 20 | 20.8 | 0.062 | 0.300 | 15.0 | 10.0 | 3.0 | 6.4 | 9.2 | 0.7 | 19.3 | 16.2 | 15.5 | 33.2 | 47.8 | 3.5 | 1.2 |
| 1887 | 50 | 18.2 | 0.110 | 0.240 | 12.4 | 11.5 | 1.4 | 7.8 | 5.8 | 1.2 | 16.2 | 12.5 | 8.6 | 48.0 | 35.8 | 7.6 | 2.0 |
| 1888 | 6 | 1.58 | 0.140 | 0.162 | 16.0 | 8.5 | 6.4 | 6.1 | 7.2 | 1.2 | 20.9 | 18.7 | 30.6 | 29.2 | 34.4 | 5.0 | 0.5 |
| 1889 | 14 | 20.5 | 0.043 | 0.410 | 14.4 | 10.0 | | 4.4 | 11.0 | 1.5 | 16.9 | 13.5 | | 26.0 | 65.0 | 9.0 | 0.6 |

* Anions dissolved from KCl treatment.

in replaceable sodium, and a minor variation was obtained in the second calcareous horizon. Sampling was made from a vertical face, making it possible to obtain a representative sample of a definite horizon; it is felt that the samples thus collected from a small alkali tract differ mainly in the extent of

TABLE 2

*Concentration of anions and cations leached from soils one year after percolation had begun. (Expressed in milliequivalents per 100 cc. of solution)*

| LABORATORY NUMBER | $SiO_3$ | Cl | $SO_4$ | $CO_3$ | $HCO_3$ | Mg | Ca | K | Na | TOTAL ANIONS | TOTAL CATIONS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1767 | 0.046 | 0.020 | 0.002 | 0.240 | 0.775 | 0.218 | 0.040 | 0.175 | 0.786 | 1.08 | 1.22 |
| 1798 | 0.043 | 0.016 | | 0.056 | 0.397 | 0.230 | 0.223 | 0.031 | 0.117 | 0.512 | 0.60 |
| 1868 | 0.066 | 0.044 | 0.088 | 0.450 | 0.935 | 0.434 | 0.067 | 0.200 | 1.03 | 1.58 | 1.73 |
| 1878 | 0.054 | 0.020 | | 0.080 | 0.536 | 0.375 | 0.252 | 0.032 | 0.208 | 0.29 | 0.85 |

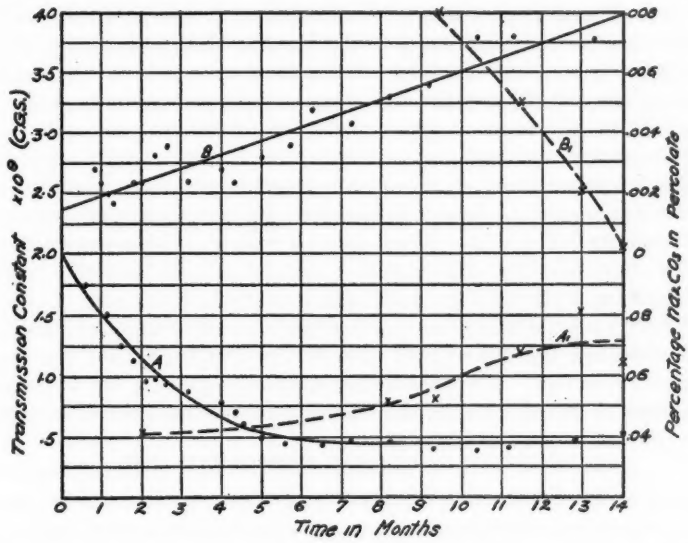


FIG. 1. *A* AND *B* TYPICAL TIME CURVES FOR THE RATE OF PERCOLATION (READ LEFT ORDINATE)

$A_1$ and $B_1$ alkalinity of percolate for the same time interval computed as percentage $Na_2CO_3$ (read right ordinate). Note: Two scales.

chemical weathering or the extent to which sodium in the soil solution had replaced calcium and magnesium from the exchange complex.

Chemical analyses were made on all samples for soluble salts, total carbonate, and replaceable bases (table 1). Percolating cans 12 cm. in diameter and 38 cm. long with a capacity of 4 kgm. of air-dry soil, were set up in triplicate, the height of water at intake and outlet so arranged as to give no pressure head.

Representative time curves for the rate of percolation of water containing approximately 35 p.p.m. of Ca through soil columns with different amounts of replaceable sodium are shown in figure 1. The downward trend in curve *A* is due to the decrease in soluble salts and subsequent hydrolysis of sodium from the colloids, producing marked alkalinity and deflocculation. This curve represents soil 1867, which contains 1 per cent soluble salts, largely sodium chloride, and is 87 per cent sodium saturated. After two months' leaching, the percentage of sodium chloride in the extract computed from the chlorine titration was 0.096. After 10 months this value was reduced to 0.024, accompanied by an increase in the alkalinity of the percolate (curve $A_1$). The experimental curves (A and $A_1$) for the limited time, seem to indicate that the lowest value of $k$ has been reached, or in other words, the final state of dispersion has been obtained. A similar analysis for all the soils makes it possible to identify a characteristic transmission constant with a definite sodium saturation. A different trend is obtained for soils that are low in replaceable sodium (curve B). This sample was considerably lower in soluble salts (0.22 per cent), and 18 per cent sodium-saturated. The gradual increase in the transmission constant is associated with the marked reduction in the alkalinity of the percolate (curve B). Since a larger percolation rate maintains (nine times as fast as in the former case), the result will be a rapid disappearance of replaceable sodium from the system. It is to be noted that the percentage of sodium carbonate is approaching a zero concentration on the fourteenth month (see upper scale on right ordinate), but the percolate is well on the alkaline side of neutrality; thus, there is a reason to believe that the soil will continue to improve with leaching, $k$ getting larger until a maximum value is obtained.

The percolation studies were made in triplicate columns and the conductance of the percolate, together with the transmission constant, was observed over a long period of time. Any appreciable variation in the rate due to channels developing in the soil mass can be detected by the conductance measurement.

## METHOD OF DETERMINING REPLACEABLE BASES

In view of the uncertainty of determining accurately replaceable bases in calcareous soils, it seems necessary to explain briefly the method used. The common ammonium chloride method will not suffice for calcareous soils because of the solubility effects of silicates and carbonates of calcium and magnesium. These difficulties, accompanied with a high concentration of soluble salts whose removal affects the exchangeable constituents, make it reasonable to expect inaccuracies in any method. In brief, the following procedure was adopted:

Replaceable sodium and potassium were determined from an $NH_4Cl$ treatment, since their determination and replacement are not influenced by solubility effects. However, due allowance is made for the water-soluble cations in the soil previous to treatment.

Replaceable calcium and magnesium were determined from a KCl treatment, but correct-

ing for the Ca and Mg equivalent to the loss in carbonates plus dissolved silica in the solution, assuming in the latter case a solution of a metasilicate of calcium and magnesium.

The $NH_4$ absorbed was determined by the usual method as a reasonable check on the total bases.

It is to be noted in table 1 that the correction for dissolved anions is distributed between the total Ca and Mg determinations in a definite ratio. For example, three successive comparable treatments after the replaceable divalent cations were determined gave a constant ratio of Ca to Mg in the solution, namely 4 m.e. of Ca to 1 of Mg. Therefore, by expressing dissolved $CO_2$ and $SiO_2$ in m.e. per 100 gm. and dividing the sum in the ratio of 4 to 1, the correction can be made from total Ca and Mg determination and the relative amounts of the replaceable divalent cations can be obtained. It should be pointed out that this is only a suggestive possibility for distributing the solubility effect and has no bearing on the experimental relations here considered. For in this work an accurate measure of the total bases was desired so that the ratio of replaceable sodium to the total could be obtained with the same degree of accuracy.

In connection with the KCl treatment, it is to be noted that the solution of carbonates and silicates is greater in an $NH_4Cl$ treatment than in a KCl treatment. Thomas (3) reports an approximate threefold increase in dissolved silicates, and a fivefold increase in dissolved carbonates where $NH_4Cl$ was used as the displacing agent, as compared with KCl or NaCl. Under these conditions a KCl treatment will give a more complete replacement of Ca and Mg. This is illustrated in table 1. The total amount of bases determined exceeds the amount of $NH_4$ absorbed by consistent amounts, except where the soil is practically Na saturated, and here the agreement is better. This shows that in the absence of replaceable Ca and Mg equivalent absorption and replacement of Na and K can be analytically realized.

The constant presence of dissolved calcium during the $NH_4Cl$ treatment not only prevents the replacing action from going to completion, but it is likely that Ca ion is acting as the displacing cation instead of $NH_4$. This point is emphasized because sample 1876 gave 18.2 m.e. of Na and K replaced with a less equivalent absorption of ammonia.

## DISCUSSION OF RESULTS

From the experimental data in figure 2 it would seem that a logarithmic relation between $k$ and $S$ will approximate the facts. The permeability obtained from varying a single factor ($S$) can be expressed in curves which are asymptotic to a minimum. The empirical relation is obtained by the ordinary method of plotting $ln\ k$ against $S$ and evaluating the constants. The extreme high and low values of $S$ are extrapolated, but the experimental range from $S$ equals 12 to 87 includes the major part of the curve. Comparing the two relations obtained from the surface and $CaCO_3$ horizons, one is led to conclude that the calcareous horizon when free from alkali, or in the best

physical condition, is more impervious than the surface 18 inches. On the other hand, being a more compact soil in an alkali-free condition, the latter horizon will respond more slowly to corresponding increments in $S$ resulting in a higher percolation rate at saturation. In this connection it may be noted that Greenville soil is very loamy and permeable ($k = 30 \times 10^{-9}$) in the normal Na-free conditon, but when treated with NaCl and washed free from salts the value of $k$ decreases to $0.3 \times 10^{-9}$. This is the same order of magnitude obtained in the foregoing for a heavier clay soil. In this case only the two extreme values can be given and not the complete curve.

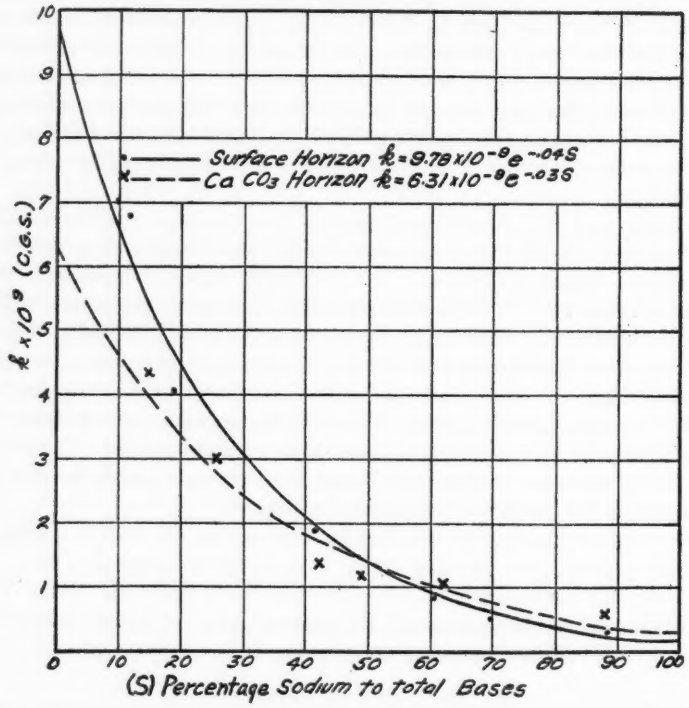


FIG. 2. RELATION BETWEEN TRANSMISSION CONSTANT AND PERCENTAGE OF SODIUM FOR TWO HORIZONS

Reference has been made by Kelley and Brown (2) to the effect that a calcareous soil saturated with replaceable sodium can be reclaimed without chemical treatment by leaching and drainage. Burgess (1) has also shown that the reclamation of calcareous alkali soil by leaching only (without applying gypsum) is possible, but it is an extremely long and tedious process unless irrigation water high in soluble calcium is available. This slowness is due to the extremely low solubility of $CaCO_3$ in alkaline soil solutions. The gradual

change of replaceable sodium into replaceable calcium during leaching has been shown by various investigators, but the length of time required to bring about a quantitative change is our immediate concern. The solution of this problem centers around the setting up of a differential equation containing the necessary variables. Seemingly, a differential equation is necessary since the sodium will disappear from the solid phase and hence be leached out at a variable rate as a result of the changing concentration and percolation rate as time goes on. If the rate at which the replaceable sodium disappears from a homogeneous soil column is proportional to the total replaceable Na present (which would seem to harmonize with the generalized law of mass action) and at the same time is proportional to the permeability of the soil, the following differential equation to express this hypothesis may be used:

$$-\frac{dC}{dt} = KCk \qquad (A)$$

where $C$ = total exchangeable sodium in a given soil column (4 kgm.), $k$ = transmission constant (in C.G.S. units), $K$ = proportionality factor, and $t$ = time (seconds). The importance of permeability as a variable factor cannot be overemphasized, because the degree of hydrolysis and the extent of replacement of sodium by calcium are determined by the rate of dilution. The soluble products (NaOH) from hydrolysis, $Na_2CO_3$ and $NaHCO_3$ from Ca replacement) must be removed before the reaction will continue with any rapidity.

In order to obtain a solution to equation $(A)$, it is necessary, first, to express $k$ in terms of $C$, and, second, to determine the proportionality constant by measuring experimentally the derivative for different values of $C$. This would give some assurance as to the validity of the expression over a wide range. Since $C$ and $S$ are related by the expression $(A')$ $S = \frac{C}{C_t}$ where $C_t$ is equal to the total amount of replaceable bases, and assumed constant for a given soil, it follows that

$$\frac{dS}{dt} C_t = \frac{dC}{dt} \qquad (B)$$

By eliminating $C$ and $\frac{dC}{dt}$ from equation $(A)$ by using equations $(A')$ and $(B)$ the following differential equation[4] is obtained:

$$\frac{dS}{dt} = K_1 Sk; \text{ where } K_1 = -K \qquad (C)$$

By expressing $k$ in terms of $S$ from the experimental relation shown in figure 2, the following equation is obtained:

[4] The negative sign was used in the first place because $C$ decreases and consequently $S$, as the time increases.

$$\frac{dS}{dt} = K_1 S\ 9.78 \times 10^{-9}\ e^{-.04\,S} \qquad (D)$$

or

$$K_1\ 9.78 \times 10^{-9}\ dt = \frac{e^{.04\,S}\ dS}{S} \qquad (E)$$

Integrating equation (E) will give the following functional relation between $t$ and $S$:

$$K_1\ 9.78 \times 10^{-9}\ t = ln\ S + .04\,S + \frac{.04^2\,S^2}{2\,.\,2!} + \frac{.04^3\,S^3}{3\,.\,3!} + \ldots. \qquad (F)$$

This series converges rapidly because of small numerical values of $S$, and, since definite limits will be used, the integration constant vanishes. After $K$ is evaluated in equation $(F)$, it remains to substitute any desired limits in

TABLE 3

*Values of* $\frac{dc}{dt}$, $C$, $k$, *and* $K^1$ *for four soils*

| LABORATORY NUMBER | $k$ | $C$ | $\frac{dc}{dt}$* | $K^1$ |
|---|---|---|---|---|
| 1767 | $1.2 \times 10^{-9}$ | 8.16 | $2.31 \times 10^{-8}$ | 2.36 |
| 1868 | $0.77 \times 10^{-9}$ | 11.70 | $2.00 \times 10^{-8}$ | 2.21 |
| 1878 | $4.10 \times 10^{-9}$ | 2.22 | $1.97 \times 10^{-8}$ | 2.16 |
| 1798 | $6.4 \times 10^{-9}$ | 1.11 | $1.63 \times 10^{-8}$ | 2.30 |

* $\frac{c^2 - c_1}{Seconds}$ or total grams of replaceable Na that disappeared from a 4-kilogram soil column per second.

$S$ and calculate the time in seconds necessary to effect such a reduction in replaceable Na.

The constant $K_1$ was obtained from the original supposition as given in equation $(A)$ by measuring corresponding values of $\frac{dC}{dt}$, $C$, and $k$ (table 3). When the values obtained for soils containing different amounts of replaceable sodium are compared, it is evident that the proportionality constant varies within narrow limits; this is principally because of the experimental method of measuring $\frac{dC}{dt}$. These data constitute an experimental verification of the original assumption. The rate of Na replacement was determined by analyses of the percolate for total anions and cations (table 2). The total Na determination was reduced by the sodium equivalent to the chlorides and sulfates and the remainder was assumed to have come from the soil colloids. This reduction is noticeably small because the analysis was made about a year after percolation had begun. The question still

remains as to whether replaceable Na is disappearing at a finite and measurable rate, of course, realizing that it would be desirable to measure this average rate over a small time interval. Ample Na for a determination can be obtained from one month's leaching, and it is felt that the difference in the values of $C$ at the beginning and end of the month divided by $t$ in seconds, will approximate the derivative with all the accuracy that would be consistent with the previous analysis of the problem. This average rate for the time interval considered can be interpreted for all practical problems as an actual instantaneous rate, especially in view of the fact that very little

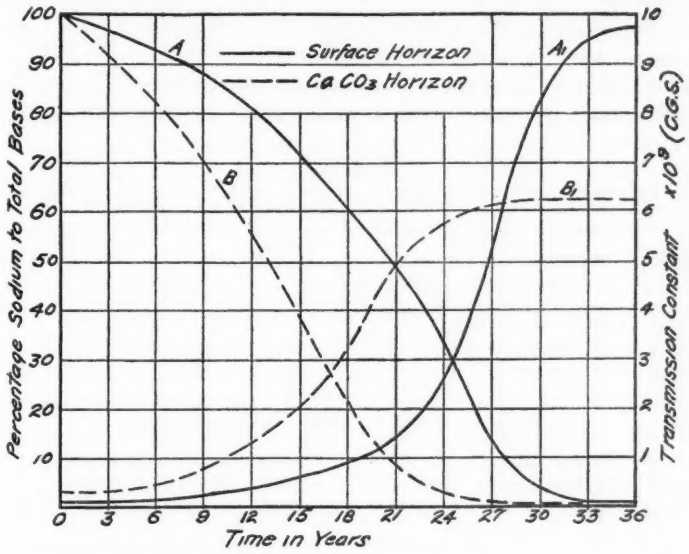


FIG. 3. *A B* CHANGE IN SODIUM PERCENTAGE WITH THE TIME (READ LEFT ORDINATE) AND $A_1$ $B_1$ SHOWS INCREASE IN THE RATE OF PERCOLATION WITH THE TIME (READ RIGHT ORDINATE)

or no measurable change in $k$ would result from a 20 to 50 mgm. reduction in replaceable Na from a soil column containing 6 to 16 gm.

The results of table 2 also emphasize the rôle soluble calcium plays during the leaching. Such large differences in the calcium content of the percolates cannot be due to a difference in the solubility of calcium carbonate. Moreover, the low calcium values from the highly sodium-saturated soils seems to be due to the replacement of Na by Ca and subsequent formation of large quantities of sodium carbonate and sodium bicarbonate. This reaction is going on in the other samples which are low in replaceable Na and where high Ca extracts were obtained, but to a less extent because of the limited amount of replaceable Na present.

A clear interpretation of equation ($F$) can be obtained from figure 3 (see curve A). A similar equation involving the experimental relation for the $CaCO_3$ horizon, which changes only the constants, gives curve B. This curve has a greater slope for large values of $S$, which is due to a larger percolation rate at saturation resulting in a greater net amount of soluble products removed. For convenience the ordinate was shifted in order that 100 per cent would correspond to zero time in each case. The corresponding curves (A and B) involving the transmission constant as a function of the time were deduced from equation ($F$) and the analogous equation for the $CaCO_3$ horizon, by expressing $S$ in terms of $k$. These curves give a complete time history of the transmission constant until replaceable Na is reduced to a point where its presence or absence from a soil mass has little or no influence upon the transmission constant. It would require more than 20 years to verify these curves experimentally, but it is of interest to note that the experimental curve B in

TABLE 4

*Reduction in replaceable Na due to continuous leaching under field conditions*

| LABORATORY NUMBER | RELATIVE PROPORTIONS IN SURFACE HORIZON | | | | | LABORATORY NUMBER | RELATIVE PROPORTIONS IN $CaCO_3$ HORIZON | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ca | Mg | Na | K | AVERAGE PER CENT Na | | Ca | Mg | Na | K | AVERAGE PER CENT Na |
| 1893 | 33.4 | 15.8 | 40.0 | 10.8 | | 1894 | 33.3 | 6.0 | 60.1 | 0.6 | |
| 1897 | 45.0 | 16.5 | 34.0 | 4.5 | | 1898 | 16.9 | 21.7 | 53.0 | 8.4 | |
| 1903 | 43.2 | 32.0 | 23.0 | 1.8 | 32.3 | 1904 | 15.7 | 28.6 | 49.4 | 6.7 | 54.8 |
| *Results for comparable samples after 2 years' leaching* | | | | | | | | | | | |
| 1895 | 54.0 | 16.7 | 21.0 | 8.3 | | 1896 | 33.7 | 28.2 | 38.1 | 0.6 | |
| 1899 | 49.4 | 34.6 | 16.0 | | | 1900 | 32.1 | 23.3 | 37.9 | 8.4 | |
| 1901 | 63.1 | 21.2 | 12.3 | 3.4 | 16.4 | 1902 | 24.4 | 38.4 | 31.5 | 6.7 | 35.8 |

figure 1 has approximately the same slope as the theoretical curve A in figure 3 would demand. That is to say, when the transmission constant is in the neighborhood of $3.0 \times 10^{-9}$, the rate at which it increases is of the order of magnitude that the calculation gives.

A comparison of the time values here given with reduction in replaceable Na, resulting from leaching conditions in the field, can be obtained from table 4. A few years ago on this alkali tract small pressure wells were drilled into the gravel stratum, with the thought of measuring artesian pressure. After 2 years of continuous flowing, soil samples were taken from the surface and $CaCO_3$ horizons in the immediate vicinity of the wells. The analysis for replaceable bases on the leached and unleached soils is shown in table 4. The results from three different locations are averaged in each case because sampling was more or less at random. As a result of 2 years' leaching with artesian water, evidently replaceable Na has been reduced in the surface horizon from 32.3 to 16.4 per cent and in the $CaCO_3$ horizon from 54.8 to 35.8 per cent.

Referring to the former curves, figure 3, one obtains approximately 2.3 and 2.7 years, respectively, for corresponding reductions. Obviously, field and laboratory conditions are not closely comparable. Under field conditions there are at least four factors influencing the results and which do not exist under laboratory conditions:

The liberation of $CO_2$ by decaying organic matter, furnishing a better solvent for the solution of $CaCO_3$.

Surface run-off carrying injurious alkalinity.

Higher Ca content in the water used, which was especially true in this case.

Fresh water is not applied to the lower horizon. The leachings from the surface soil will contain Na ions which will tend to retard the ionization of Na zeolites. However, this retarding effect, in part or wholly, may be compensated for by the first factor.

These factors, together with the experimental results, seem to point toward a faster reclamation under field conditions, which is more encouraging.

From the data here presented and discussed it is evident that the relation between replaceable sodium and soil permeability harmonizes with the contention held by various investigators, namely, that as Na is substituted for the normally occurring calcium in the exchange complex the soil becomes less and less permeable to water. Also, if the substitution goes very far marked alkalinity will be produced. There is no critical danger point, but the effect is highly pronounced at 30 per cent saturation, increasing at a slower rate thereafter. The decrease in permeability soon begins to manifest itself in highly Na-saturated soils, as was pointed out in figure 1, curve A. No single case was encountered where water penetration ceased altogether, even in soil samples taken from slick spots which most writers would pronounce as 100 per cent Na saturated. Although this may be the case in non-calcareous soils, as various investigators have shown, it is felt that for calcareous soils a finite and measurable rate of percolation maintains. This argument may be advanced in favor of the reclamation of calcareous alkali soils by flooding and drainage, whereas a non-calcareous soil would require the application of a chemical treatment.

## SUMMARY

Studies on calcareous soils to determine a relation between soil permeability and replaceable Na show that the permeability decreases exponentially as the Na content increases.

When free from alkali that soil higher in humus is more pervious than the calcareous horizon. The reverse is true, however, when the soils are Na saturated.

The effect of long-time leaching on replaceable sodium and soil permeability is deduced. The time values given in figure 3 serve as a guiding theory for the reclamation of calcareous alkali soils. For the surface horizon and leaching with water containing approximately 35 p.p.m. of calcium, one obtains 18.8 years as the time required to reduce replaceable sodium from 88 to 10

per cent. A corresponding reduction for the calcium carbonate horizon could be realized in 15.6 years. Seven years would be required to obtain a reduction from 50 to 10 per cent.

Data are presented to show the reduction in replaceable Na as a result of continuous leaching under field condition. The results indicate that a faster rate of reclamation is possible under field conditions than is indicated by the laboratory work. The data, however, are not voluminous enough to obtain a factor by which the rates given in figure 3 could be discounted and obtain a value that would be comparable to field conditions.

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# REPLACEABLE IRON AND ALUMINUM IN SOILS

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The researches of Magistad (8), Joffe and McLean (5, 6), and others have shown that the presence and amount of soluble iron and aluminum in soils are dependent upon the hydrogen-ion concentration of the soil solution and upon the nature, and possibly also the concentration, of the anions present. Our knowledge of the factors that determine the soil content of replaceable iron and aluminum, however, is less well defined. For example, it is known that iron and aluminum do not always appear in the filtrate when acid soils are extracted with a neutral salt solution, but the circumstances which determine their presence or absence are somewhat obscure. Further, although Mattson (9) has demonstrated that iron and aluminum may continue to be replaced from the soil material as often as it is rendered unsaturated, yet the relationship which the quantity of trivalent ions bears to the state of unsaturation of the soil remains uncertain. In addition, doubt exists as to whether replacement is direct, through exchange with the cations of the neutral salt used, or indirect through interaction with released hydrogen ions.

For these reasons a study has been made of the influence exerted by certain factors upon the soil content of these replaceable bases. The following soil factors have been investigated: pH value and content of replaceable hydrogen.

## SOILS EXAMINED

The soils examined belong to two distinct types: soil type B—a fawn-colored river alluvium; soil type C—a red-weathering clay. The pH values and contents of replaceable hydrogen of the soils of both types cover a wide range.

Some of the physical and chemical constants of the types are recorded in table 1. The determinations were made on samples obtained by bulking the individual soils for which data are given in table 2. Organic matter was measured by the method described by Hardy (3), and clay by the pipette procedure adopted in 1928 by a Sub-Committee of the Agricultural Education Association (13).

Additional information concerning the types may be obtained elsewhere (14).

Soil types B and C are predominantly siliceous. Both are deficient in organic matter. Their saturation capacities, clay contents, and moisture contents at the point of stickiness indicate that both types are highly colloidal.

Examination of the individual soils has shown that each type is fairly uniform in character. The extent to which the various samples differ in their content of organic matter and clay does not appear large enough to exert an appreciable disturbing effect upon the amounts of replaceable iron and aluminum which they may contain.

## EXPERIMENTAL

*The pH values* of the soils and soil extracts were determined by means of the quinhydrone electrode. In the former case a ratio of soil to water of 1 to 2 was used.

*Replaceable iron and aluminum* were measured on 50-gm. representative samples of the air-dried, soils, which were treated with hot normal sodium chloride solution, stirred, allowed to stand overnight, decanted several times, transferred to funnels, and leached.

Joffe and McLean (6) have shown that iron and aluminum may continue to be replaced from soils, by repeated extraction with normal barium chloride solution, until the filtrate attains a pH value of 5.4 to 5.6. After 1 liter of

TABLE 1

*Some constants of the soil types examined*

| SOIL TYPE | $\frac{R_2O_3}{SiO_2}$ | $\frac{Fe_2O_3}{Al_2O_3}$ | LOSS ON IGNITION | ORGANIC MATTER | CLAY | SATURATION CAPACITY | M.P.S. |
|---|---|---|---|---|---|---|---|
| | | | *per cent* | *per cent* | *per cent* | *m.e.** | *per cent* |
| B | 0.58 | 0.73 | 13.58 | 1.07 | 68.9 | 24.2 | 46.1 |
| C | 0.43 | 0.44 | 11.76 | 1.28 | 50.6 | 24.3 | 39.0 |

M.e. = milligram equivalents per 100 gm. soil.

extract had been obtained, small samples of the filtrate still leaching through were therefore examined for the presence of trivalent ions. Aluminum was present in a number of cases, but iron was invariably absent. The occurrence of aluminum in the filtrate samples was shown to be dependent on their pH value. Aluminum ceased to be displaced by the first liter of sodium chloride solution only when the filtrate samples had attained a pH value of 6.5 to 6.6, a hydrogen-ion concentration approximately one-tenth as great as that recorded by Joffe and McLean (6). The discrepancy is probably due to the difference in the nature of the replacing cation used, and possibly also to a difference in concentration of the chloride ion in the leaching solutions.

The soils which still contained aluminum replaceable by this process were transferred to beakers, and again decanted and leached with normal salt solution. Replacement was found to cease when an additional half liter of filtrate had been obtained, except in the case of the most highly acid and unsaturated soils. The amount of aluminum present in the third half-liter in some cases exceeded 0.7 m.e. per 100 gm. of air-dry soil.

The iron and aluminum present in each filtrate were separately determined,

due precautions being taken to remove any manganese and other metals, and any silica and phosphate present.[1] The trivalent bases were also weighed together as ignited oxides. The data obtained by the two methods showed close agreement.

*Replaceable hydrogen* was determined indirectly on 25-gm. samples of the soils. Exchangeable calcium was measured by the method of Hissink, and saturation capacity by leaching to 2 liters according to a method based on that

TABLE 2

*pH value, content of replaceable iron, aluminium, and hydrogen; and thiocyanate color of soils examined*

| SOIL TYPE B | | | | | | SOIL TYPE C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Soil number | pH value | Replaceable | | | KCNS color* | Soil number | pH value | Replaceable | | | KCNS color* |
| | | Fe | Al | H | | | | Fe | Al | H | |
| | | *m.e.* | *m.e.* | *m.e.* | | | | *m.e.* | *m.e.* | *m.e.* | |
| M 48 | 6.55 | Trace | 0.14 | 8.25 | 0 | M101 | 7.51 | 0.00 | 0.00 | 5.46 | 0 |
| M 28 | 6.50 | 0.00 | 0.00 | 6.25 | 0 | M 64 | 7.14 | 0.00 | 0.00 | 4.21 | 0 |
| M 46 | 6.42 | 0.00 | 0.00 | 4.54 | 0 | M 96 | 6.87 | 0.00 | 0.00 | 3.64 | 0 |
| M 27 | 5.79 | Trace | 0.11 | 9.25 | 2 | M163 | 6.74 | 0.00 | 0.00 | 4.50 | 0 |
| M 22 | 5.63 | Trace | 0.22 | 9.00 | 5 | M157 | 6.67 | 0.16 | 0.11 | 12.11 | .... |
| M 24 | 5.31 | 0.00 | 0.00 | 7.54 | 23 | M100 | 6.61 | 0.00 | 0.00 | 4.89 | 0 |
| M 25 | 4.93 | Trace | 0.33 | 12.50 | 45 | M 71 | 6.07 | 0.00 | 0.00 | 6.54 | 0 |
| M 44 | 4.92 | Trace | 0.56 | 14.61 | 25 | M 67 | 5.87 | Trace | 0.33 | 8.46 | .... |
| M 49 | 4.75 | 0.10 | 0.50 | 13.96 | 36 | M160 | 5.60 | Trace | 0.11 | 11.61 | 7.5 |
| M 45 | 4.65 | 0.15 | 2.67 | 17.32 | 50 | M123 | 5.50 | Trace | 0.33 | 8.25 | .... |
| M 30 | 4.58 | Trace | 2.48 | 15.96 | 62 | M155 | 5.08 | 0.00 | 0.22 | 15.29 | 30 |
| M 29 | 4.53 | Trace | 0.33 | 12.86 | 46 | M158 | 5.08 | 0.16 | 0.56 | 16.64 | 36 |
| M 23 | 4.53 | Trace | 4.83 | 17.50 | 60 | M164 | 4.98 | 0.16 | 0.39 | 9.86 | 31 |
| M180 | 4.38 | 0.16 | 2.26 | 16.61 | .. | M161 | 4.95 | 0.04 | 0.22 | 14.54 | 35 |
| .... | .... | .... | .... | ..... | .. | M165 | 4.77 | Trace | 2.18 | 17.32 | 41 |
| .... | .... | .... | .... | ..... | .. | M159 | 4.55 | 0.16 | 3.44 | 19.68 | 64 |
| .... | .... | .... | .... | ..... | .. | M156 | 4.48 | 0.00 | 5.20 | 20.21 | 50 |

* Based on an arbitrary unit.

of Page and Williams (14). An estimate of the soil content of replaceable hydrogen, or saturation deficit, was obtained by difference.

The data thus obtained are recorded in table 2.

## DISCUSSION AND CONCLUSIONS

### *Replaceable iron*

Mere traces of iron were replaced from the majority of soils examined. Measurable amounts, which in no case exceeded 0.2 m.e. per 100 gm. of soil,

[1] The procedure followed was devised by Mr. H. H. Croucher, formerly of the Imperial College of Tropical Agriculture, Trinidad, to whom the author is indebted for the details of the method.

were found more frequently in the red-weathering clays than in the alluvial soils. The occurrence of replaceable iron in such meager quantity is in common with the experience of other workers (2, 6).

In the case of the soils of type B, iron first becomes replaceable in determinable amount at a pH value of 4.75 and at a saturation deficit of 14 m.e. With type C the corresponding pH and deficit values are 6.67 and 10 m.e., respectively. Replaceable iron was found to be absent, or present in traces only, however, in many soils with lower pH values and higher saturation deficits. In consequence, no well-defined relationship is evident between the quantities of iron present in the filtrates and either of these soil factors.

*Replaceable aluminum*

The maximum amount of aluminum, replaceable by the treatment described, in the soils of types B and C is 5.2 m.e. In other Trinidad soils as much as 30.7 m.e. have been found. Smolik (12) has shown 13.5 m.e. to occur in soils of the podzol type, Joffe and McLean (6) 14.5 m.e. in New Jersey soils, and Conrey and Schollenberger (2) 2.1 m.e. in a Clermont silt loam subsoil.

The large amounts of aluminum, relative to those of iron, which are replaceable from the soils of types B and C may be of considerable importance in determining the nature of the end products of the weathering processes to which these soils are subject.

Theoretically, the sum of the equivalents of the replaced iron and aluminum should be considered in relation to the pH values and saturation deficits of the soils examined. As the amounts of iron contribute little or nothing to the sum totals of the trivalent bases, they have been neglected in the main discussion which follows.

*pH value*

The hydrogen-ion concentrations of the soils are plotted against their contents of replaceable aluminum in figure 1.

Although there is a general tendency for the amount of aluminum to increase with increasing hydrogen-ion concentration, the points do not fall even approximately upon a smooth curve. Aluminum is invariably absent from the filtrates obtained from the soils with pH values between 7.5 and 6.7, but always appears when the pH value of the soil lies below 5.1. It may or may not be present over the pH range 6.7 to 5.1. At pH values greater than 4.8 the quantity of replaceable aluminum does not exceed 0.6 m.e. At pH values smaller than this it may rise rapidly, but irregularly, in amount.

The hydrogen-ion concentration of the soil, therefore, does not appear to be the only factor of consequence which controls the presence and amount of replaceable aluminum. A similar conclusion can be drawn from the data recorded by Conrey and Schollenberger (2) which are included in figure 1 for the purpose of comparison.

The consistent appearance of replaceable aluminum at pH values below 5.1 in the soils of both series is of interest, for, according to Pryanishinikov and Lukovnikov (10), the aluminum ion is not adsorbed by soils with pH values greater than 5.0. It is possible, therefore, that aluminum becomes directly exchangeable in the region of this hydrogen-ion concentration.

This view is to some extent confirmed by the fact that, without exception, the soils of pH value less than 5.1, *whether their contents of replaceable aluminum were large or small*, alone needed leaching to more than 1 liter to ensure complete replacement. Slow replacement is to be expected if aluminum is present in the exchangeable form, for the trivalent aluminum ion, because of its rela-

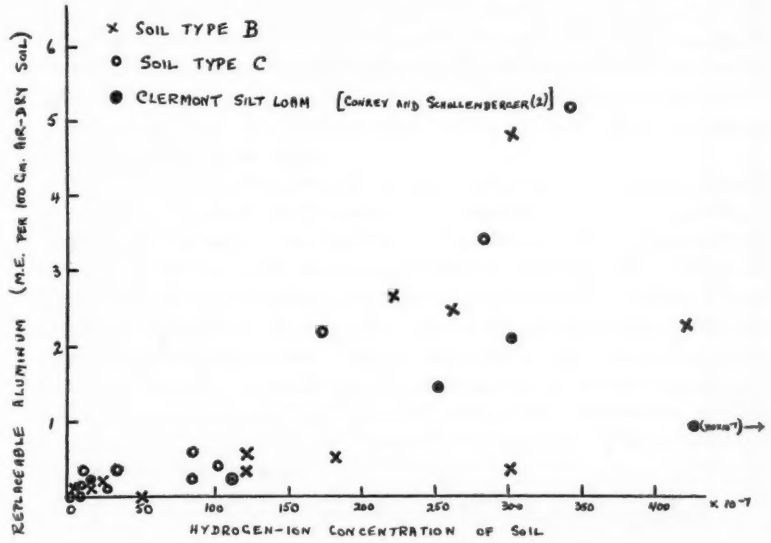


FIG. 1. RELATIONSHIP BETWEEN HYDROGEN-ION CONCENTRATION AND CONTENT OF REPLACEABLE ALUMINUM OF SOIL

tively low electro-affinity, would be replaced with difficulty by sodium ions. On the other hand, when exchange is entirely indirect through interaction with released hydrogen ions, replacement would not only be more rapid, but would tend to take place in the earlier stages of the leaching process, i.e., at the time when the filtrate possesses its maximum hydrogen-ion concentration.

It is worthy of note that Magistad (8) found the amount of aluminum present in the soil solution to increase rapidly at pH values below 4.8

### *Replaceable hydrogen*

The saturation deficits of the soils examined are plotted against the amounts of replaceable aluminum in figure 2.

It will be seen from this figure that:

(*a*) The amount of replaceable aluminum bears a fairly close relationship to the soil content of replaceable hydrogen.

(*b*) The points tend to fall on two smooth curves, which may be distinct, and which correspond to the two soil types.

The data recorded by Conrey and Schollenberger (2), when similarly plotted, give rise to a third curve. It should be mentioned, however, that these workers used a normal solution of ammonium acetate as the leaching agent, and measured replaceable hydrogen by electrometric titration of the filtrate.

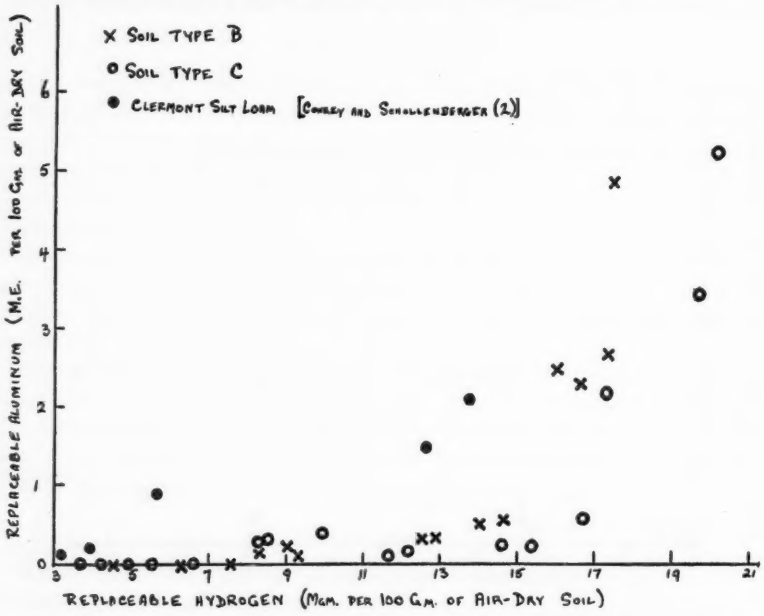


Fig. 2. Relationship Between Soil Content of Replaceable Hydrogen and Aluminum

The existence of a different curve for each soil type is to be expected, for the data of Burgess (1) indicate that the amounts of aluminum dissolved by dilute acid from soils of approximately equal pH value, but belonging to different types, may vary greatly. Further, the degree of dehydration of the alumina gel in soils, which many consider to be the main source of the replaceable aluminum, may vary with soil type, and in consequence may exhibit different degrees of reactivity towards acid.

(*c*) Replaceable aluminum is not found in the filtrate until the saturation deficit attains a minimum value of 8.25 m.e.

The existence of such a minimum value suggests that a definite hydrogen-

ion concentration must be attained by the filtrate before aluminum becomes replaceable. It provides an explanation of the lack of consistency in the occurrence of aluminum in the filtrates obtained from soils with pH values greater than 5.1.

(*d*) The curves fall into two portions, one of which corresponds to the range of saturation deficit 8.25 to 15.5 m.e. and the other to the range 15.5 to 21 m.e. Between 8.25 and 15.5 m.e. each curve approximates to a straight line, the amount of aluminum replaced being small. When the deficit exceeds a value of 15.5 m.e. a very rapid and fairly regular increase is evident in the quantity of aluminum.

A saturation deficit as large as 15.5 m.e. is found only in the soils with pH values less than 5.1. It therefore appears probable that the amount of aluminum present in the normal salt extract is completely dependent on the magnitude of the saturation deficit, provided the pH value of the soil is greater than 5.1, and that, under such circumstances, the aluminum is replaced by indirect means alone. On the other hand, both direct and indirect replacement may occur at lower pH values.

It is unlikely that the curve for indirect replacement continues indefinitely as a straight line when the saturation deficit exceeds 15.5 m.e. It is difficult, therefore, to distinguish the aluminum which is indirectly replaceable from highly acid soils from that which may be directly exchangeable. As the total amount of aluminum replaced from such soils is more closely related to saturation deficit than to the pH value (fig. 1 and 2), the former is probably the more important controlling factor. This is borne out by the rapid fall in the content of replaceable aluminum which accompanies a decrease in saturation deficit (e.g., compare soil M 29 with M 23 and M 30). Presumably, therefore, the major portion of the aluminum passes indirectly into solution even in the soils of lowest pH value.

Similar considerations probably hold for the replacement of iron. In this case, however, a larger saturation deficit (10 to 12 m.e.) is needed before the base becomes indirectly exchangeable in measurable quantity. Also, as iron, when replaceable, passes into solution in the earlier stages of the leaching process (none was found in the filtrate samples taken at the end of the first liter stage of the extraction), and as no marked increase is evident in the contents of iron of the filtrates from the most acid soils, it is doubtful whether any of the soils of types B and C possess a pH value low enough for it to be present in the directly exchangeable form. Such a state of affairs would be in accordance with the results of Joffe and McLean (5), who found that iron is precipitated from solution at a higher hydrogen concentration than is aluminum.

It has been suggested that the aluminum passes into the salt extract as colloidal hydrous oxide from soils with pH values approaching neutrality. Under certain circumstances this assumption may be largely correct. Nevertheless, in view of the relationship which obtains between the initial appearance of aluminum in the filtrate and the magnitude of the saturation deficit

under stringent conditions of filtration, and as the filtrate attains its maximum hydrogen-ion concentration very rapidly (7), the importance of the assumption may be over-emphasized.

The extent to which the aluminum present in the filtrate could be responsible for the exchange acidity of the soils examined is a matter of some interest. The value of the ratio of replaced hydrogen to aluminum is of the order of 50 for soils with saturation deficits between 8.25 and 15.5 m.e. At greater deficits the ratio falls rapidly, reaching a minimum of 3.6 in soil M 23. The amount of aluminum in the filtrate is therefore not even approximately equivalent to the saturation deficit in the case of any of these soils, but the trend of the curves in figure 2 indicates that a state of equivalence is likely to exist in soils possessing slightly larger deficits than those recorded. These results are not in agreement with the theory that the replaced aluminum can account for the exchange acidity of soils of intermediate, rather than low, pH value.

### *Degree of unsaturation*

As the necessary data were available, the relationship between the degree of unsaturation of the soil (14) and its content of replaceable aluminum was also investigated. The amounts of aluminum in the filtrates from the soils of both types were found to be smaller than 0.60 m.e. until the degree of unsaturation exceeds 60 per cent, when the aluminum increases substantially but irregularly in quantity. In all other respects the measure of correspondence between the two factors is small.

## THIOCYANATE REACTION

Suggestions have been made, notably by Hissink (4), that the intensity of color developed when soils are treated with an alcoholic solution of potassium thiocyanate may be used as an indication of their degree of acidity. Saint (11), however, has shown that the relationship is not uniform in character. He ascribes the inconsistences to variation in the iron and organic matter contents, and to the texture, of the soils he examined.

In view of the practical value of the thiocyanate test, and its widespread use, advantage has been taken of the data accumulated to reinvestigate in more detail the relationship between the color intensity and certain soil factors.

The following procedure was used for determining thiocyanate color: 1-gm. samples of soil were shaken with 5 cc. of a 40 per cent alcoholic solution of potassium thiocyanate for 5 minutes. The suspensions were allowed to settle for 48 hours and the intensity of color developed was compared with that of standard solutions containing known amounts of iron. The figures obtained, which are based on arbitrary units, are set out in table 2.

### *Replaceable iron*

In the soils examined the measure of correspondence between thiocyanate color and the amounts of iron replaced is small.

As traces only of iron were found in the majority of the filtrates an attempt was made colorimetrically to determine the amounts present, to enable them to be correlated with thiocyanate color. The attempt was unsuccessful, as the colors given by the filtrates in most cases were too faint to be differentiated accurately.

*pH value*

The soils with pH values greater than 6.0 gave no coloration with potassium thiocyanate. Those with pH values smaller than 6.0 gave a color, irrespective of the magnitude of their saturation deficits.

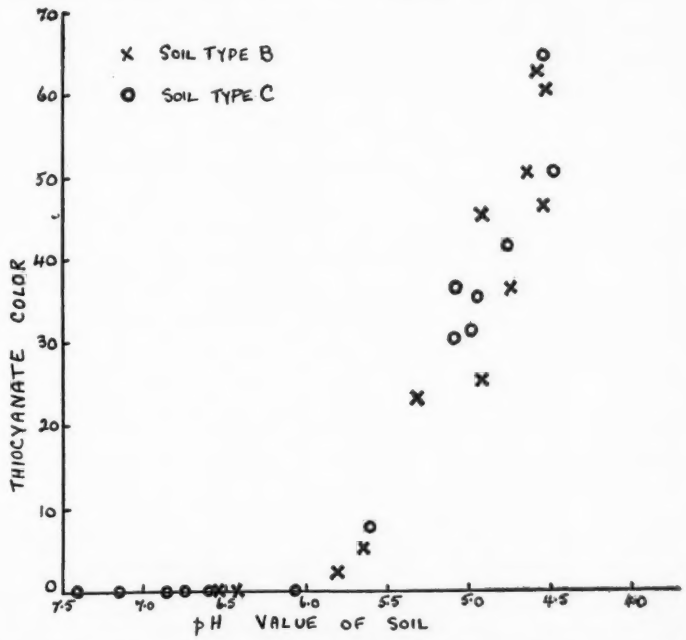


FIG. 3. RELATIONSHIP BETWEEN pH VALUE OF SOIL AND THIOCYANATE COLOR

The relationship between pH value and thiocyanate color is very close (fig. 3). The points fall on a straight line over the whole range of pH values recorded, for which colors are evident. The correlation between intensity of color and pH value is $-0.938$ for the 18 soils giving a positive reaction, $P$ being smaller than 0.01.

When thiocyanate color is plotted against hydrogen-ion concentration as such, the tendency of the curve to bend over toward the hydrogen axis becomes marked in the region of an ion concentration of $1 \times 10^{-5}$ (pH 5).

### *Replaceable hydrogen*

The relationship between thiocyanate color and saturation deficit also appears linear (fig. 4), but it is not as well defined as that which holds for pH value.

The correlation coefficient between thiocyanate color and saturation deficit is + 0.761, with $P$ less than 0.01.

### *Discussion*

The lack of correspondence between the amounts of replaceable iron and thiocyanate color indicates that the conditions controlling replacement in the

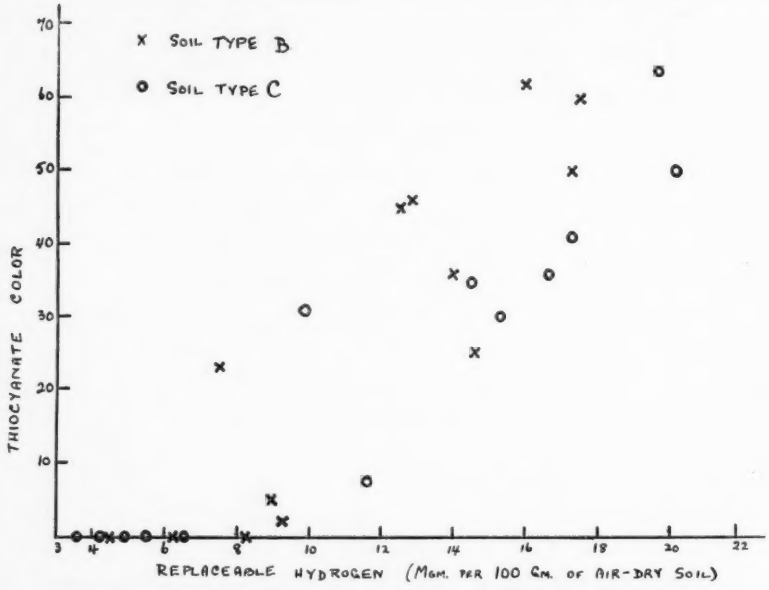


FIG. 4. RELATIONSHIP BETWEEN SOIL CONTENT OF REPLACEABLE HYDROGEN AND THIOCYANATE COLOR

presence of sodium chloride and potassium thiocyanate differ materially. The high concentration of the thiocyanate solution, and the formation of a very slightly ionized ferric salt in this case, are undoubtedly contributing factors, for they tend to bring about maximum replacement under the conditions of the experiment, and to minimize the effect of disturbing influences due to the presence of other ions.

The relation between thiocyanate color and pH value at first sight appears anomalous. The high degree of correspondence is probably due to the fact that no attempt is made in the thiocyanate reaction to drive replacement to completion by continued leaching with fresh solution. In consequence, the

thiocyanate color is less dependent on the total exchange acidity of the soil, and more dependent on its immediately available acidity, than would be the case under the conditions of normal exchange procedure. The use of an alcoholic solution probably emphasises such a state of affairs by depressing the degree of ionization of the soil complex.

Statistical analysis of the data recorded lends confirmation to this view. The partial correlation coefficient between thiocyanate color and pH value, when allowance is made for saturation deficit, is $-0.853$ ($P = <0.01$). This value does not differ significantly from the total correlation coefficient. The partial correlation coefficient between color intensity and saturation deficit, pH value being constant, is $+ 0.215$ ($P = >0.1$). pH value is therefore undoubtedly more important than total saturation deficit (as measured by the method described) in determining thiocyanate color. The direct correlation coefficient between color intensity and saturation deficit over-estimates the degree of correspondence between these factors.

The multiple correlation coefficient between thiocyanate color, and pH value and saturation deficit, which measures, in a sense, the extent to which color intensity is related to their combined variation, is 0.941.

## SUMMARY

An examination has been made of the influence which the hydrogen-ion concentration and the state of unsaturation of the soil exert upon its content of replaceable iron and aluminum. It has been found that:

Replaceable aluminum is invariably present only in soils with pH values less than 5.1. The relationship between the hydrogen-ion concentration of the soil and the quantity of replaceable aluminum is very irregular.

The amount of replaceable aluminum appears closely related to the magnitude of the saturation deficit. Aluminum is not found in the filtrate until the deficit attains a minimum value of 8.25 m.e. Until the deficit reaches 15.5 m.e., it increases slowly in quantity. Above 15.5 m.e. the increase is extremely rapid.

The amount of aluminum replaced at any given saturation deficit may vary with soil type.

Indications exist that replacement of aluminum is wholly indirect in soils with pH values greater than 5.1 (the maximum recorded pH value corresponding to a saturation deficit of 15.5 m.e.). At lower pH values direct replacement may also occur, but indirect replacement appears to predominate.

Between the deficits 8.25 and 15.5 m.e. the ratio of replaceable hydrogen to aluminum is of the order of 50. The rapid fall in the ratio at greater deficits suggests that the replaced aluminum may be equivalent in amount to the exchange acidity in highly unsaturated soils.

The measure of the relationship between the amount of replaceable aluminum and the degree of unsaturation of the soil is small.

Iron does not appear in measurable quantity in the filtrate until the saturation deficit attains a value of 10 to 12 m.e. None of the soils examined appear to possess a pH value low enough for iron to become directly exchangeable.

The relationship between thiocyanate color and soil acidity has been reinvestigated. It has been found that the intensity of color is more closely related to the pH value of the soil than to the saturation deficit.

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# THE DETERMINATION OF LIME REQUIREMENT BY THE DIRECT ADDITION OF CALCIUM CARBONATE

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Since calcium carbonate is the material used most generally for the correction of soil acidity, it would seem that the best estimate of the lime requirement of a soil could be made in the laboratory by the use of $CaCO_3$.[2] Jensen (9), who used lime water and changed the excess to $CaCO_3$ by passing $CO_2$ through the soil supension stated that a nearer approach to natural conditions would be made if the soils were mixed directly with $CaCO_3$ or a solution of $Ca(HCO_3)_2$. Biroux and Pien (2) added the calculated amount of lime and three times the calculated amount to samples of soil in the laboratory and after making them up to optimum moisture let them stand. The results showed a slow reacidification, some soils becoming more acid than at the start, after standing 8 weeks. Mattson (12), using an electrodyalized Sharky colloidal material (11) placed his 1-gm. samples in conical bags of thin parchment paper with enough water completely to saturate and cover the soil. The bags were then placed in a soft paste of pure $CaCO_3$ and at intervals of 1, 3, 7, 8, and 14 days a bag was removed and its contents tested for adsorbed calcium. Seven days were required for equilibrium when the soil material was completely unsaturated.

Crowther and Martin (6) added 2 gm. of $CaCO_3$ to 0, 10, 20, 30, and 40 gm. of soil in uniform 275-cc. bottles, filled the bottles with water and a drop or two of toluene and after shaking 16 hours let them sit for a day or two till reasonably clear. Then they determined the total carbonic acid both as free and as bicarbonate and found it to be greater than that estimated by the Hutchinson-MacLennan method.

Demalon (7) obtained pH 7.1 by adding powdered $CaCO_3$ to the soil suspension in a Knight shaking electrode where the $CO_2$ was eliminated by the bubbling H.

## EXPERIMENTAL

Several 60-gm. samples of the soil, which was air-dry and had been passed through a 1-mm. sieve, were weighed out. To these were added varying

[1] From the department of agricultural and biological chemistry. Published by permission of the director as Scientific Contribution 33 of the New Hampshire Agricultural Experiment Station.

[2] The author is indebted to Professors R. M. Salter of the Ohio Agricultural Experiment Station and T. G. Phillips of this station for this suggestion.

amounts of c.p. $CaCO_3$, from 0.06 gm., representing 1 ton of $CaCO_3$ to the acre of soil weighing 2,000,000 pounds, to 0.48 gm. representing 8 tons of $CaCO_3$ to the acre. In order to maintain the same water relation as is used in the electrometric determinations of pH, 60 cc. of water was added to each sample. In the first experiment mixing was accomplished in tightly stoppered 250-cc. wide-mouth bottles using an end-over-end shaker. The course of the reaction was followed by determining the pH of the suspension by the quinhydrone electrode. Equilibrium was reached in 20 to 24 hours. The results for the method samples are shown in curve I, figure 1. As the failure to obtain neutrality was

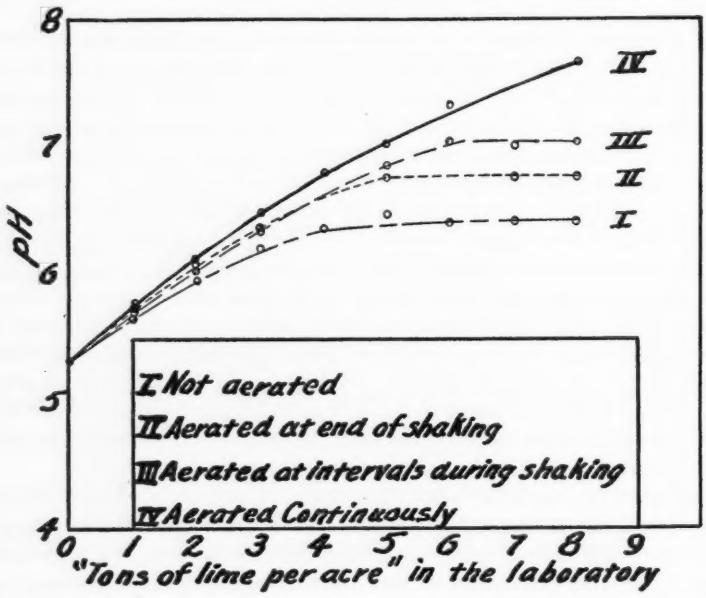


FIG. 1. THE EFFECT OF AERATION ON THE TITRATION CURVES WHEN $CaCO_3$ IS USED

probably due to the accumulation of $CO_2$, an upright shaker was used, the bottles were left unstoppered, and the suspension was aerated.

Curve II, figure 1, was obtained by this method with aeration only at the end of the shaking period; curve III with aeration at intervals during the shaking.

Finally, in order to remove $CO_2$ as fast as it was formed, the equipment shown in plate 1 was used. The air drawn through the series of funnels by a water aspirator was passed through water before entering the first funnel in order to avoid drying out the sample in the first funnel. The stopcocks were adjusted so that sufficient air passed through to keep the soil in motion and to prevent the soil suspension from entering the stems of the funnels. Equilibrium was reached in about 20 hours. The results obtained are readily reproducible. Curve IV, figure 1, illustrates the results with the method sample.

This method was used on the soils listed in table 1. The results are presented in table 2 and the titration curve for soil IV, highly buffered, and soil II, poorly buffered, are shown in figure 2. The lime requirement was calculated

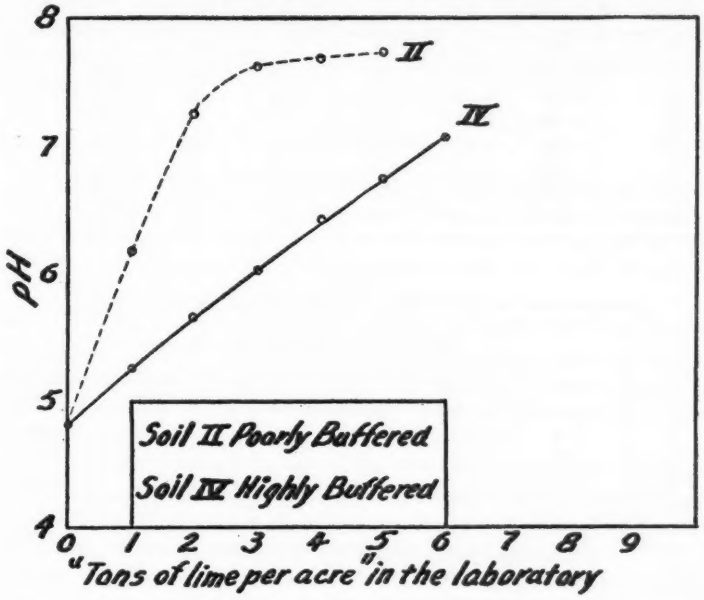


FIG. 2. TITRATION CURVES OF TWO SOILS THAT DIFFER IN ORGANIC MATTER

TABLE 1

*Description of the soils used in this experiment*

| NAME OF FARM | NUMBER OF SOIL | TYPE OF SOIL | | | pH |
|---|---|---|---|---|---|
| | | Sand | Silt | Clay | |
| | | *per cent* | *per cent* | *per cent* | |
| Adams | I | 20.0 | 25.4 | 54.6 | 5.186 |
| Carter | II | 68.3 | 17.7 | 14.0 | 4.837 |
| Currier | III | 74.7 | 9.7 | 15.6 | 5.894 |
| Jackson | IV | 47.2 | 26.0 | 26.8 | 4.805 |
| Livingstone | V | 47.4 | 33.7 | 18.9 | 5.634 |
| Redden | VI | 71.0 | 10.4 | 18.6 | 5.650 |
| Whenal | VII | 57.9 | 20.4 | 21.7 | 4.873 |

by interpolation as the number of tons of $CaCO_3$ required to bring 2,000,000 pounds of the soil to pH 7.0.

The lime requirement of these soils was determined also by the following methods: pH as determined by the quinhydrone electrode in a 1–1 water sus-

TABLE 2

*The results obtained in the laboratory from the use of $CaCO_3$*

| NUMBER OF SOIL | TONS OF LIME IN LABORATORY | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
| | *pH* | *pH* | *pH* | *pH* | *pH* | *pH* | *pH* |
| I | 5.186 | 5.648 | 6.071 | 6.414 | 6.867 | 7.227 | |
| II | 4.837 | 6.196 | 7.248 | 7.632 | 7.706 | 7.741 | |
| III | 5.894 | 6.445 | 6.950 | 7.356 | 7.690 | 7.871 | |
| IV | 4.805 | 5.250 | 5.670 | 6.038 | 6.408 | 6.721 | 7.075 |
| V | 5.634 | 6.162 | 6.712 | 7.161 | 7.558 | 7.696 | |
| VI | 5.650 | 6.244 | 6.754 | 7.221 | 7.631 | 7.724 | |
| VII | 4.873 | 5.487 | 5.931 | 6.319 | 6.692 | 7.044 | |

TABLE 3

*A comparison of the results obtained by different lime requirement methods*

| SOIL | TONS OF $CaCO_3$ AS DETERMINED BY THESE TESTS | | | | | |
|---|---|---|---|---|---|---|
| | $CaCO_3$ | Truog | Jones | pH* | Hydrolytic acidity | Exchange acidity |
| I | 4.4 | 4.0 | 3.4 | 4.3 | 3.9 | 0.7 |
| II | 1.8 | 2.0 | 1.6 | 3.8 | 1.9 | 0.3 |
| III | 2.1 | 1.5 | 2.1 | 1.25 | 2.2 | 0.05 |
| IV | 5.8 | 4.0 | 3.9 | 4.5 | 4.5 | 0.3 |
| V | 2.6 | 1.0 | 2.3 | 2.5 | 2.6 | 0.0 |
| VI | 2.5 | 1.0 | 2.1 | 1.75 | 2.8 | 0.1 |
| VII | 4.9 | 3.0 | 3.4 | 4.0 | 4.2 | 0.5 |

* Lime requirement as determined by the pH was based on the type of soil as determined by the Bouyoucos hydrometer method (1) and a table prepared by Morgan (13), using alfalfa as the test crop.

TABLE 4

*The results obtained in the field from the application of ground limestone*

| NUMBER OF SOIL | TONS OF LIME IN FIELD | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | 4 | |
| | pH | L. F.* | pH | L.F. | pH | L.F. | pH | L.F. |
| I | | | 5.70 | 1.6 | | | | |
| II | 5.63 | 1.30 | 6.08 | 2.22 | 6.39 | 2.55 | | |
| III | 6.52 | 0.87 | | | | | | |
| IV | | | 5.54 | 1.45 | | | 5.81 | 1.66 |
| V | 5.91 | 1.90 | 6.18 | 1.90 | | | | |
| VI | | | 6.25 | 2.00 | | | | |
| VII | | | 5.97 | 0.98 | | | 6.42 | 1.23 |

* L.F. = liming factor.

pension, Truog (18), Jones (8), hydrolytic acidity (10), and exchange acidity (10). The last two were calculated on the basis of an acre of soil weighing 2,000,000 pounds. The results obtained are given in table 3.

The results of the addition of ground limestone in the field to the soils studied are presented in table 4. These figures represent the maximum change which occurs in most of the cases 2 years after application and which agrees with Rost and Fieger (15).

## DISCUSSION

The results in table 3 show a marked difference in the amount of lime to be added as determined by the various methods. Runk (16) compared the Comber, Truog, and sodium acetate tests and obtained varying results. Since these tests measure different forms of acidity a difference would be expected. The $CaCO_3$ method is used as a basis of comparison.

The Truog method gives lower results, with the exception of soil II. This soil was low in organic matter. There was more than a ton's difference on some of the farms, and as these results were consistently low and since there was a personal element involved in reading the color, the Truog was considered unsatisfactory.

The Jones method also gave low results even though the factor 1.8 was used. However, this may be due to the need of a larger factor for New Hampshire soils. The results are better than with the Truog method, and, with a factor that varied with the type of soil, better results would be obtained.

The lime requirement as determined by the pH was based on the type of soil as determined by the Bouyoucos hydrometer method (1) and a table prepared by Morgan (13), using alfalfa as the test crop. The results are for the most part better than the Jones method with the exception of soil II, which is 2 tons too high.

The hydrolytic acidity results agreed best with the $CaCO_3$ figure. As in the Jones test, calcium acetate was used, but the longer and more thorough mixing with the soil, together with the different method of calculation, accounts for the improved results.

From the exchange acidity results it is evident that New Hampshire soils contain very little exchange acidity and in the majority of cases it can be disregarded as a factor to be considered when a field is to be limed. Biroux and Pien (2) found the exchange acidity as determined by the Daikuhara method to be in the great majority of cases 10 to 20 times lower than the electrometric and Hutchinson method.

The $CaCO_3$ method was carried out with field experiments as standards [cf. Jensen (9) and Crowther (4)]. Jensen (9) found that he had to multiply his laboratory results by three in order to obtain the same effect in the field, which gave him a "liming factor" of 3. Pierre and Worley (14), who limed pots in the greenhouse with amounts of $CaCO_3$ based on the soils' exchange hydrogen, did not obtain pH 7 and decided that either the $CaCO_3$ reacted with other materials

or not all acid was determined. They also stated that the non-exchangeable soil complex was believed to be responsible for the presence of the "liming factor" of 1.5 which they obtained. Crowther (5) believed that the liming factor was due to considerable movement of lime into the subsoil.

Table 4 shows the field results and the liming factors. Since the soils were not limed to pH 7.0 the factors were figured for the actual pH obtained. Conner, Walker, and Plice (3) had to use 12 tons of limestone to obtain pH 7.1 on a Clermont silt loam, and with a Newton sandy loam 16 tons gave them only pH 6.5. Our field results tend in the same direction and since good yields can be obtained without completely neutralizing the soil [cf. Slipher (17), Runk (16), and Conner, Walker, and Plice (3)], one can, by using the liming factor and laboratory curve, lime to a definite pH under 7.0. As shown in table 4 the liming factor varies with the different soils and with different amounts of lime in the same soil.

Soil II, which had the steepest laboratory curve (fig. 2), gave the greatest "liming factor." However, there was a definite increase in the weight of silage corn grown on this field with each added ton of lime. The soil being sandy and poorly buffered, one would expect more change in pH in the field. The subsoil has not been checked and the lime may have been carried there or passed through as nitrate, sulfate, and chloride [cf. Conner, Walker, and Plice (3)].

For the most part the factor varies between 1 and 2. Soils III and VI, which are both high in sand but with VI having more organic matter, have factors of 0.87 and 2.00 respectively. Soils IV and V, which are fairly high in organic matter also have a high factor whereas soil VII, which is low in organic matter, has a factor near 1.0. Soil I is very high in clay, which acts as a buffer, and has a factor similar to a soil that is high in organic matter.

## SUMMARY

A method of obtaining the lime requirement by the direct use of $CaCO_3$ has been described.

From interpolation on the laboratory curve and by the use of a factor depending on the amount of organic matter, it is possible to calculate how much lime to apply in the field in order to obtain a definite pH. This is a decided advantage as it is not necessary to lime to pH 7.0., and various crops require different pH values.

The $CaCO_3$ method agrees favorably with the hydrolytic acidity method for determining lime requirement.

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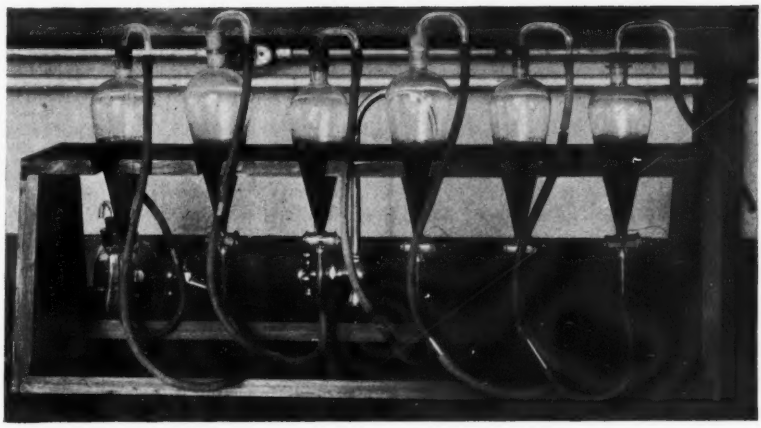
PLATE 1

THE EQUIPMENT USED TO MIX THE $CaCO_3$ WITH THE SOIL SUSPENSION



# EFFECTS OF SORGHUM PLANTS ON BIOLOGICAL ACTIVITIES IN THE SOIL

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Fortunately, the conditions necessary for the normal development of the majority of higher plants and the beneficial forms of microorganisms in the soil are approximately the same. Experiments have definitely proved that neither group of organisms can function normally for any extended period of time without the other. All life is dynamic and subject to the influences of many other things, of which one of the more important is other types of life. That growing plants and microorganisms in the soil may affect each other, either favorably or unfavorably, is now an accepted fact. Some of the relationships between the two groups of organisms have been demonstrated satisfactorily, whereas others are, as yet, but incompletely worked out and not well understood.

Starkey (8) recently discussed the relationships between higher plants and microorganisms in the soil and gave a comprehensive review of the literature on the subject. The review of literature shows that the evolution of carbon dioxide is greater from soils that support plant growth and that the amounts of gas produced depend on the kinds of plants and the character of their growth. Maximum effects have been found at advanced stages of vegetative development and fruiting. Correlated with carbon dioxide production are numbers of microorganisms which are increased on the roots and in the vicinity of the roots of many crops, the most striking increases being in the *B. radiobacter* group, although the general bacterial population, actinomycetes, and filamentous fungi all show increases. Plant roots have been found to excrete soluble organic substances and the increased numbers of oganisms on and near the roots appear to be due, largely, to root excretions and not to decaying root cells. The presence of legumes apparently stimulates bacterial activities in the soil to a greater extent than the presence of non-legumes, this being especially true of nitrification.

There are few data concerning the effects of sorghum plants on the biological and chemical activities in the soil. The following work with kafir, corn, wheat, and barley was undertaken to determine whether sorghums affect soil activities more or less than corn or other crops.

## EXPERIMENTAL

Studies were carried on in both cropped and fallowed soils and determinations were made of carbon dioxide evolution, the nitrate content of the soils, the hydrogen-ion concentration of the soil solutions, the total numbers of filamentous fungi and other microorganisms (bacteria and actinomycetes), the water-soluble organic matter and water-soluble phosphorus content of the soil solution, and the nitrifying, nitrate assimilating, and nitrogen fixing powers of the soils.

The plants were grown in 4-gallon earthenware pots in the greenhouse. Clarion loam was used, each pot containing approximately 30 pounds. Four pots were planted to each of the four crops and four were left unplanted. Half of the pots were used for biological and chemical studies and the other half for carbon dioxide determinations. When the plants had developed sufficiently for the elimination of the weaker ones they were thinned, three corn or kafir plants and 21 wheat or barley plants being left in the respective pots.

The soils were kept near the optimum moisture content except for a few days prior to sampling, when water was withheld to allow the soils to become dry enough to permit sampling with a tube. After samples were taken, soil from the surface of the pot was worked and pressed into the holes and the moisture content was brought to optimum again. Soil, of the original supply, was added occasionally after sampling to keep the pots full and prevent exposure of the roots.

As the period of daylight at the time of planting was short, the pots were grouped in circles under reflectors having 500-watt Mazda bulbs. During December and the early part of January the lights were turned on in the late afternoon and turned off about 11 o'clock at night. The barley plants grew normally and corn responded well to the light, but wheat had a tendency to grow rapidly without the production of tillers. Kafir showed a marked indifference to the added light, although, judging from work with plants during the preceding winter, the increased amount of light kept the plants growing and prevented early maturity.

The barley plants were attacked by the powdery mildew, *Erysiphe graminis*, and were treated with powdered sulfur. All of the pots were dusted with sulfur so that comparative results could be obtained.

Soil samples for biological and chemical determinations were taken from the one group of pots at intervals of two weeks throughout the periods of growth and at maturity of the corn, wheat, and barley. The last soil samples were taken from the kafir pots when the plants were in full bloom. Soil samples were obtained by means of a small brass tube with an inside diameter of 12 mm. From 18 to 20 samples were taken from each pot. No attempt was made to obtain the samples under aseptic conditions, as the errors due to contamination were regarded as negligible.

The following methods were used in making biological observations and chemical determinations on the soils:

In the study of carbon dioxide evolution, samples of the soil atmosphere were obtained by means of glass aspirator bulbs surrounded with glass wool and buried in the soil about 2 inches above the centers of the bottoms of the pots. The bulbs were connected by means of glass and rubber tubing to a simplified Haldane apparatus which employed 50 per cent potassium hydroxide solution as the carbon dioxide absorbent.

The phenoldisulfonic acid method, as modified by Harper (3), was used in determining nitrate nitrogen.

The quinhydrone electrode was used in determining pH values.

Soil dilutions and plate counts of microorganisms were made according to the methods recommended by Waksman (10, 11). Sterile physiological salt solution (8.5 gm. of sodium chloride in a liter of distilled water) was used instead of tap water in making the dilutions.

Sodium albuminate agar (2, medium 5) was used in making plate counts of bacteria and actinomycetes.

Determinations of numbers of filamentous fungi were made with peptone-glucose acid agar (2, medium 18). The medium was adjusted to pH 3.8–4.0. Calculated amounts of *N*. $H_2SO_4$ were added before sterilization, no trouble being experienced in obtaining a firm medium of the desired pH value.

The method described by Bondorff and Christensen (1) was employed in making the determinations of water-soluble organic matter. Fifty grams of soil and 500 cc. of distilled water were used to obtain the filtrate.

Water-soluble phosphorus determinations were made according to the Deniges method, as modified by Parker and Fudge (6). The solutions for the tests were obtained by placing the equivalent of 25 gm. of air-dried soil and 50 cc. of distilled water inside a collodian bag. The bag was then immersed in 200 cc. of distilled water and the soil was dialyzed from 30 to 42 hours.

## CARBON DIOXIDE EVOLUTION

The soils used in making the carbon dioxide determinations had stood in the pots throughout the previous summer and had become quite dry. They were planted on December 4 and the first carbon dioxide determinations were made on December 5. The dates of sampling and the results obtained are shown in table 1. The addition of water to the more or less dry soil at the beginning of the experiment brought about increased microbiological activities and a marked increase in carbon dioxide in the soil air. The amounts of carbon dioxide increased gradually until the maximum was reached, in most cases, on the third day. From then on there was a gradual decrease until January 30, when the lowest levels were reached. During the period from December 4 to December 30 the percentage of carbon dioxide in the soil atmosphere varied widely and there were, apparently, very minor effects from the plant roots. From December 30 to February 2 the amounts of carbon dioxide found in the soils varied, but the differences were not marked. There was evidence that the growing plants, with the exception of kafir, were causing increases in the amount of carbon dioxide. Beginning with February 2, when wheat and barley were heading and the corn tasseling, it was evident that all plants were bringing about increases in the amounts of carbon dioxide. The largest amounts of carbon dioxide were found under corn. Wheat had about the same effects as barley. The results obtained with kafir fluctuated widely until April 6, when marked increases in the amounts of carbon dioxide produced became evident.

TABLE 1

*Carbon dioxide in the soil atmosphere under corn, kafir, wheat, barley, and fallow*

| CROP | PERCENTAGE BY VOLUME OF CARBON DIOXIDE AT DIFFERENT DATES OF SAMPLING | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | December 5 | December 6 | December 7 | December 8 | December 9 | December 10 | December 11 | December 12 | December 14 | December 16 | December 18 | December 20 | December 22 | December 24 | December 30 | January 5 | January 12 |
| Corn | 3.75 | 5.60 | 6.00 | 7.20 | 5.80 | 6.00 | 3.80 | 2.60 | 1.40 | 0.95 | 0.25 | 0.35 | 0.35 | 0.25 | 0.10 | 0.20 | 0.30 |
| Corn | 4.40 | 5.80 | 5.60 | 4.90 | 3.20 | 2.80 | 1.40 | 0.90 | 0.60 | 0.40 | 0.20 | 0.15 | 0.20 | 0.20 | 0.05 | 0.20 | 0.20 |
| Kafir | 3.50 | 4.30 | 3.90 | 3.00 | 1.70 | 1.80 | 0.80 | 0.60 | 0.40 | 0.40 | 0.15 | 0.15 | 0.17 | 0.22 | 0.02 | 0.17 | 0.17 |
| Kafir | 4.20 | 5.80 | 5.30 | 4.40 | 2.40 | 2.40 | 1.00 | 0.70 | 0.45 | 0.40 | 0.20 | 0.20 | 0.15 | 0.25 | 0.10 | 0.20 | 0.17 |
| Wheat | 3.10 | 4.00 | 4.20 | 3.80 | 3.40 | 3.85 | 2.60 | 2.00 | 1.35 | 0.60 | 0.30 | 0.20 | 0.20 | 0.22 | 0.10 | 0.17 | 0.20 |
| Wheat | 3.60 | 4.80 | 5.00 | 4.70 | 4.20 | 4.15 | 2.40 | 1.70 | 0.95 | 0.60 | 0.20 | 0.20 | 0.25 | 0.25 | 0.10 | 0.15 | 0.22 |
| Barley | 3.80 | 5.30 | 5.70 | 5.20 | 5.00 | 5.25 | 3.00 | 1.80 | 0.70 | 0.60 | 0.20 | 0.20 | 0.20 | 0.20 | 0.10 | 0.17 | 0.30 |
| Barley | 3.60 | 4.80 | 4.60 | 4.00 | 3.00 | 2.75 | 1.45 | 1.00 | 0.60 | 0.25 | 0.20 | 0.15 | 0.25 | 0.22 | 0.05 | 0.25 | 0.25 |
| Fallow | 4.20 | 4.60 | 3.60 | 2.40 | 1.40 | 1.05 | 0.50 | 0.25 | 0.20 | 0.15 | 0.10 | 0.15 | 0.20 | 0.17 | 0.05 | 0.25 | 0.20 |
| Fallow | 3.45 | 4.90 | 4.70 | 5.40 | 4.10 | 5.10 | 3.70 | 2.75 | 1.70 | 1.05 | 0.35 | 0.40 | 0.40 | 0.40 | 0.05 | 0.17 | 0.17 |

| CROP | PERCENTAGE BY VOLUME OF CARBON DIOXIDE AT DIFFERENT DATES OF SAMPLING | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | January 19 | January 26 | February 2 | February 9 | February 16 | February 23 | March 2 | March 4 | March 9 | March 16 | March 23 | March 30 | April 6 | April 13 | April 24 | May 3 | May 8 |
| Corn | 0.22 | 0.30 | 1.80 | 0.60 | 1.30 | 1.62 | 0.42 | 1.20 | 2.40 | 1.85 | 1.45 | 0.90 | 2.30 | 1.45 | 1.10 | .... | .... |
| Corn | 0.20 | 0.20 | 0.90 | 0.90 | 1.35 | 1.00 | 0.25 | 1.20 | 3.20 | 1.75 | 1.40 | 0.77 | 1.80 | 1.60 | 1.30 | .... | .... |
| Kafir | 0.15 | 0.10 | 0.35 | 0.20 | 0.80 | 0.55 | 0.20 | 0.42 | 0.55 | 0.80 | 0.75 | 0.70 | 1.60 | 2.60 | 0.85 | 0.95 | 0.90 |
| Kafir | 0.15 | 0.15 | 0.37 | 0.20 | 0.75 | 0.45 | 0.22 | 0.60 | 1.00 | 0.75 | 0.85 | 0.80 | 1.40 | 1.90 | 1.05 | 1.35 | 1.25 |
| Wheat | 0.20 | 0.22 | 0.40 | 0.57 | 1.60 | 0.37 | 0.10 | 0.40 | 0.42 | 0.50 | 0.60 | .... | .... | .... | .... | .... | .... |
| Wheat | 0.22 | 0.20 | 0.80 | 0.55 | 1.00 | 0.42 | 0.15 | 0.60 | 0.82 | 0.50 | 0.47 | .... | .... | .... | .... | .... | .... |
| Barley | 0.32 | 0.35 | 0.62 | 0.55 | 1.40 | 0.52 | 0.22 | 0.60 | 0.80 | 0.55 | 0.55 | .... | .... | .... | .... | .... | .... |
| Barley | 0.22 | 0.22 | 0.60 | 0.55 | 1.30 | 0.50 | 0.22 | 0.50 | 0.45 | 0.40 | 0.45 | .... | .... | .... | .... | .... | .... |
| Fallow | 0.10 | 0.10 | 0.17 | 0.17 | 0.20 | 0.12 | 0.20 | 0.20 | 0.05 | 0.20 | 0.20 | 0.15 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Fallow | 0.15 | 0.10 | 0.20 | 0.20 | 0.25 | 0.25 | 0.05 | 0.20 | 0.10 | 0.22 | 0.20 | 0.15 | 0.20 | 0.20 | 0.15 | 0.15 | 0.20 |

It is of interest to note the marked differences in the results obtained at times from the duplicate pots. The results obtained on March 2 are also of interest, as a very cloudy and cold period occurred at that time. The cold, cloudy weather evidently caused a depression in both plant and microbiological activitivies which was reflected in the carbon dioxide content of the soil atmosphere.

## SOIL NITRATES

Determinations for nitrates were made on 50-gm. equivalents of air-dried soil. The results are shown in table 2. The amounts of nitrates in the soils at the time of planting varied considerably. No marked changes in the nitrate content took place in the corn soils during the first eight weeks, but at the end of the tenth week or about two weeks before the plants began to tassel a decided decrease was evident. A further decrease was noted at the end of the twelfth week. From then on to harvest the soils in the duplicate pots behaved differently. The nitrate content of the kafir soils behaved in a very erratic manner, increasing to the end of the sixteenth week and then decreasing during the next six weeks. The smallest amounts were obtained at the last sampling when the plants were in full bloom. The nitrate content of the wheat pots showed considerable fluctuation from week to week, but there was no evidence of the plants having utilized large amounts at any particular period. The smallest amounts of nitrates were found about four weeks before heading and at blossoming time. The nitrate content of the barley soils was lowest at the end of the twelfth week (blossoming time) after which an increase occurred. The fallow soils gained and lost in nitrate content in an irregular way until the end of the experiment, when there was about twice as much nitrate nitrogen

TABLE 2

*Nitrate nitrogen content of soil under corn, kafir, wheat, barley, and fallow*

| CROP | NITRATE NITROGEN, P.P.M. | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | November 22 | December 6 | December 20 | January 3 | January 17 | January 31 | February 14 | February 28 | March 14 | March 28 | April 11 | April 25 |
| Corn | 49.7 | 50.0 | 47.1 | 43.5 | 50.0 | 38.2 | 31.7 | 37.2 | 40.8 | 41.6 | 40.6 | .... |
| Corn | 41.8 | 41.3 | 41.3 | 41.3 | 38.4 | 25.6 | 10.8 | 11.2 | 5.9 | 11.1 | 18.5 | .... |
| Kafir | 38.8 | 43.4 | 45.4 | 41.9 | 47.6 | 47.6 | 42.2 | 49.6 | 51.0 | 43.5 | 38.5 | 25.6 |
| Kafir | 49.3 | 50.0 | 54.2 | 54.3 | 61.0 | 59.5 | 60.3 | 55.1 | 62.3 | 55.5 | 44.6 | 44.6 |
| Wheat | 34.1 | 35.9 | 37.0 | 28.6 | 38.2 | 34.9 | 32.5 | 38.1 | 51.0 | .... | .... | .... |
| Wheat | 44.9 | 49.5 | 47.1 | 41.9 | 55.5 | 47.1 | 40.0 | 52.9 | 62.3 | .... | .... | .... |
| Barley | 34.9 | 27.7 | 25.0 | 24.3 | 23.5 | 17.4 | 11.9 | 17.0 | 24.0 | .... | .... | .... |
| Barley | 38.8 | 34.8 | 33.5 | 38.4 | 32.5 | 22.0 | 22.6 | 31.8 | 52.0 | .... | .... | .... |
| Fallow | 44.2 | 48.0 | 44.6 | 50.0 | 60.9 | 58.1 | 61.5 | 66.6 | 77.7 | 71.4 | 62.5 | 71.4 |
| Fallow | 39.0 | 38.4 | 37.6 | 45.4 | 50.0 | 50.5 | 48.4 | 61.5 | 63.5 | 71.4 | 55.5 | 60.9 |

as at the beginning. It is evident that the plants made their greatest draft on soil nitrates prior to and at the time of fruit formation. Wheat did not draw so heavily on soil nitrates as did the other crops. Crop growth was evidently not heavy enough to utilize the nitrates much faster than they became available.

## HYDROGEN-ION CONCENTRATION

Hydrogen-ion determinations were made along with the other determinations and although differences were found from time to time the data did not indicate that the plants caused definite changes in pH values at any particular stage of their growth. The data in table 3 show that growing plants tend to cause a decrease in hydrogen-ion concentration compared to that of unplanted soils, corn and kafir having much greater effects than wheat or barley.

TABLE 3

*Hydrogen ion concentration of soil solutions under corn, kafir, wheat, barley, and fallow*

| CROP | pH VALUES AT DIFFERENT DATES OF SAMPLING* | | | |
|---|---|---|---|---|
| | December 4 | March 28 | April 25 | May 9 |
| Corn | 7.19 | .... | 7.41 | .... |
| Corn | 7.21 | .... | 7.70 | .... |
| Kafir | 7.18 | .... | .... | 7.51 |
| Kafir | 7.17 | .... | .... | 7.51 |
| Wheat | 7.17 | 7.12 | .... | .... |
| Wheat | 7.19 | 7.32 | .... | .... |
| Barley | 7.20 | 7.29 | .... | .... |
| Barley | 7.21 | 7.29 | .... | .... |
| Fallow | 7.19 | .... | .... | 6.92 |
| Fallow | 7.19 | .... | .... | 6.99 |

* Soil samples from $CO_2$ pots.

## NUMBERS OF BACTERIA AND ACTINOMYCETES

Bacteria and actinomycetes appeared to grow equally well on the medium used. As so many of the colonies were small, necessitating the use of the microscope to differentiate between bacteria and actinomycetes, it seemed preferable to count the two orders together rather than make a higher dilution and increase the chances for error. The numbers found at different dates of sampling are recorded in table 4.

The numbers of bacteria and actinomycetes fluctuated widely from time to time and in duplicate pots. The organisms began to increase in numbers during the latter part of January and, with few exceptions, the numbers remained relatively high until the end of the experiment. That the increased numbers were not entirely due to the influence of the growing plants is shown by the fact that marked increases occurred in the fallow soils. By averaging the numbers of bacteria and actinomycetes for 10 counts, or a period of 18 weeks,

the corn soils were found to have an average of 10,761,000 organisms per gram of soil; kafir soils averaged 9,258,000; wheat soils 9,720,000; barley soils 9,101,000; and fallow soils 8,449,000. The corn soils averaged 12,863,000 bacteria and actinomycetes per gram of soil against 9,307,000 per gram of fallow soil during a period of 22 weeks. The kafir soils were found to average 11,466,000 bacteria and actinomycetes per gram of soil, whereas fallow soils averaged 9,716,000 for a period of 24 weeks. There was a remarkably close agreement between the average results of the duplicate treatments.

The foregoing figures show that larger numbers of bacteria and actinomycetes occurred in cropped than in uncropped soils, the largest numbers being found in corn soils. Root cutting by the soil sampling tube was, undoubtedly,

TABLE 4

*Numbers of microörganisms (bacteria plus Actinomycetes) in the soil under corn, kafir, wheat, barley, and fallow*

| CROP | NUMBERS OF MICROÖRGANISMS PER GRAM OF SOIL AT DIFFERENT DATES OF SAMPLING* | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | November 22 | December 6 | December 20 | January 3 | January 17 | January 31 | February 14 | February 28 | March 14 | March 28 | April 11 | April 25 | May 9 |
| Corn | 114 | 576 | 636 | 808 | 736 | 806 | 520 | 2,428 | 2,100 | 1,962 | 2,837 | 1,924† | ..... |
| Corn | 86 | 1,034 | 596 | 696 | 748 | 1,890 | 836 | 1,604 | 1,546 | 1,802 | 2,984 | 1,604† | ..... |
| Kafir | 80 | 822 | 584 | 482 | 712 | 840 | 882 | 1,855 | 1,120 | 1,737 | 2,062 | 1,674 | 1,390† |
| Kafir | 82 | 1,132 | 632 | 638 | 566 | 736 | 1,000 | 1,950 | 1,306 | 1,360 | 3,384 | 1,460 | 1,300† |
| Wheat | 70 | 1,226 | 906 | 516 | 714 | 822 | 1,272 | 2,040 | 1,478 | 1,065† | ..... | ..... | ..... |
| Wheat | 74 | 876 | 590 | 728 | 702 | 760 | 1,057 | 2,164 | 1,496 | 885† | ..... | ..... | ..... |
| Barley | 64 | 854 | 422 | 506 | 486 | 1,206 | 1,080 | 1,916 | 1,470 | 1,130† | ..... | ..... | ..... |
| Barley | 94 | 608 | 472 | 638 | 552 | 862 | 1,440 | 1,682 | 1,227 | 1,494† | ..... | ..... | ..... |
| Fallow | 86 | 1,128 | 478 | 442 | 460 | 778 | 1,040 | 1,624 | 1,238 | 1,517 | 1,404 | 1,112 | 1,352† |
| Fallow | 54 | 882 | 476 | 482 | 382 | 626 | 1,333 | 1,166 | 1,262 | 1,444 | 1,642 | 1,282 | 1,574 |

* Ten thousands omitted.

† Soil samples from $CO_2$ pots.

responsible for part of the increases in cropped soils, but an examination of the root systems of the plants showed that root pruning had added relatively small amounts of organic matter to the food supply of the organisms at any one sampling. The root systems of the kafir plants were as well developed as, or better developed than, those of the corn plants, but fewer organisms were found under the kafir plants.

## NUMBERS OF FILAMENTOUS FUNGI

The numbers of filamentous fungi obtained by plating the soils from under the various crops are recorded in table 5. The numbers fluctuated so widely from time to time and in duplicate pots that little information can be obtained

from an examination of the table. By averaging the numbers for all periods and for duplicate pots the corn soils were found to have an average number of 29,000 per gram of soil, while the fallow soil for a similar period averaged 26,530. The kafir soil averaged 22,060 filamentous fungi per gram of soil against 27,110 per gram for the fallow soil during a period of 24 weeks. For 10 samplings, or a period of 18 weeks, the average number per gram of soil was 26,930 under corn, 20,490 under kafir, 22,260 under barley, and 23,760 in fallow soil. Apparently, the numbers of filamentous fungi increased under corn and decreased under kafir, wheat, and barley. What the effects of root pruning, in the process of soil sampling, may have been is not clear, but the effects were not marked or larger numbers of filamentous fungi would have been found in

TABLE 5

*Numbers of filamentous fungi in the soil under corn, kafir, wheat, barley, and fallow*

| CROP | NUMBERS OF FILAMENTOUS FUNGI PER GRAM OF SOIL AT DIFFERENT DATES OF SAMPLING* | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | November 22 | December 6 | December 20 | January 3 | January 17 | January 31 | February 14 | February 28 | March 14 | March 28 | April 11 | April 25 | May 9 |
| Corn | 68 | 282 | 334 | 252 | 332 | 270 | 432 | 340 | 252 | 286 | 620 | 334† | .... |
| Corn | 76 | 474 | 162 | 224 | 296 | 152 | 342 | 236 | 244 | 332 | 482 | 282† | .... |
| Kafir | 70 | 212 | 188 | 188 | 208 | 186 | 332 | 220 | 160 | 296 | 312 | 376 | 272† |
| Kafir | 60 | 168 | 174 | 190 | 184 | 202 | 228 | 254 | 174 | 204 | 456 | 206 | 216† |
| Wheat | 28 | 252 | 216 | 116 | 186 | 176 | 312 | 236 | 288 | 284† | .... | .... | .... |
| Wheat | 98 | 242 | 244 | 148 | 194 | 186 | 318 | 332 | 238 | 166† | .... | .... | .... |
| Barley | 54 | 226 | 158 | 192 | 150 | 348 | 340 | 318 | 322 | 186† | .... | .... | .... |
| Barley | 68 | 162 | 162 | 172 | 202 | 234 | 332 | 306 | 260 | 260† | .... | .... | .... |
| Fallow | 80 | 198 | 228 | 164 | 164 | 242 | 450 | 284 | 368 | 190 | 504 | 300 | 310† |
| Fallow | 56 | 290 | 162 | 158 | 210 | 222 | 426 | 258 | 376 | 226 | 654 | 246 | 284† |

* Hundreds omitted.

† Soil samples from $CO_2$ pots.

the kafir, wheat, and barley soils. The average numbers indicate that corn produced organic materials in considerable quantities and of such a quality as to cause a significant increase in numbers of filamentous fungi. No reason is offered for the decreased numbers of filamentous fungi under other crops, except that the higher plants and other organisms may have competed for certain mineral elements to the disadvantage of the filamentous fungi. Such a theory, however, appears to be untenable in the case of nitrates.

## WATER-SOLUBLE ORGANIC MATTER

The amounts of water-soluble organic matter in the soil solutions were determined every four weeks throughout the experiment. No differences were found among the soils at any one sampling, although the results varied

a little from one sampling to another. The results obtained showed no evidence that growing plants affect the amount of water-soluble organic matter in the soil. This is to be expected, for if plants do excrete readily decomposable organic substances, they would be quickly oxidized and there would be no accumulation of such materials.

### WATER-SOLUBLE PHOSPHORUS

Determinations were made every four weeks for inorganic and total water-soluble phosphorus. The soils were rich in available calcium and no trace of inorganic phosphorus could be found in any of the samples. Small differences were found in the amounts of organic phosphorus, but they were not consistent and were within the limits of experimental error. As would be expected, none of the cropped soils showed evidence of the plants having materially increased or decreased the amounts of organic phosphorus in the soil.

### NITRIFICATION, NITRATE NITROGEN ASSIMILATION, AND NITROGEN FIXATION

Determinations were made at 4-week intervals to discover what effects growing plants had on nitrification, nitrate nitrogen assimilation, and nitrogen fixation. In the nitrification studies 30 mgm. of ammonium sulfate were added to the equivalent of 100 gm. of air-dried soil and incubated 28 days. By averaging the results obtained in the nitrification studies for the various samplings from December 20 to April 11, inclusive, the increases in nitrate nitrogen were found to have been 15.38 mgm. in corn soils, 12.60 mgm. in kafir soils, and 13.43 mgm. in fallow soils. Average results from December 20 to March 14, inclusive, showed gains of 13.21 mgm. of nitrate nitrogen in wheat soils, 13.38 mgm. in barley soils, and 11.1 mgm. in fallow soils. These figures indicate a slightly increased nitrifying power in the corn, wheat, and barley soils and a decreased nitrifying power in kafir soils. Starkey (9) believed that 28 days is too long an incubation period and it is possible that differences that may have existed at an earlier period became obscured. The data obtained on the nitrate assimilating and nitrogen fixing powers of the soils likewise indicated that the growing plants had had but little effect on the nitrogen assimilating and nitrogen fixing powers of the organisms.

### DISCUSSION

The addition of water to soil which had become more or less dry has been found by many investigators to result in increased biological activities. Such was the case in this experiment, as the numbers of microorganisms found in the soils increased with the addition of water and marked evolution of carbon dioxide resulted. The activities of the organisms were at their maximum by the third day and the effects of drying the soil were evident over a period of about four weeks, as was indicated by the evolution of carbon dioxide in the soils.

After the initial high period, larger amounts of carbon dioxide were found in the planted soils and the largest amounts found in any soil occurred when the plants were most active. Growth characteristics of the plants were reflected in distinct differences in the production of carbon dioxide. The largest amounts of carbon dioxide were produced when the plants had reached advanced stages of vegetative growth. After blooming and throughout the period of grain formation the evolution of carbon dioxide was pronounced.

What factors are involved in the increased carbon dioxide formation under plants is problematical. Lundegardh (4) believed that plant roots are responsible for only one-third of the increase and that the other two-thirds are due to microorganisms. Slightly increased numbers of bacteria and actinomycetes were found in the cropped soils in these experiments. Numbers of organisms, however, are not always indicative of the rates of decomposition of organic materials, as is seen in tables 4 and 5 where large numbers of microorganisms occurred in fallow soils throughout February, March, and April without any increase in the evolution of carbon dioxide. It seems logical to conclude that part of the increased production of carbon dioxide in cropped soils is due to biological activities. If Lundegardh's contention is true, the increased amounts of carbon dioxide in cropped soils are due, largely, to a greater physiological efficiency of the organisms rather than to increased numbers. This would indicate that plant roots excrete rather large amounts of soluble organic materials which may be oxidized readily by the organisms.

What effects increased production of carbon dioxide may have had in the soils growing kafir as compared to those growing corn, wheat, or barley are not clear. The kafir plants did not develop normally, but during their period of maximum vegetative growth larger amounts of carbon dioxide were produced in the soils than in wheat or barley soils at similar stages of growth of the plants. The amounts of carbon dioxide evolved in kafir soils were but slightly smaller than the amounts found in corn soils at similar stages of growth of the plants. Metzger (5) found that the concentration of bicarbonates in soils around the roots of corn plants was not much different than in the soil about the roots of kafir plants at similar stages of development. It appears unlikely that the solubility of soil nutrients is affected to a much greater extent by the production of carbon dioxide under corn than under kafir.

The data show that the greatest disappearance of soil nitrates took place before blossoming and at the time of grain formation. There is some correlation between the evolution of carbon dioxide and the disappearance of nitrates from the soil. There appears to have been little relationship between numbers of microorganisms and nitrates found in fallow soils at any one sampling. In general, increased numbers of organisms in fallow soils were accompanied by increased amounts of nitrates. If the organisms assimilated large amounts of nitrates the production of ammonia and nitrates evidently took place at a more rapid rate. Fluctuations in the amounts of nitrates found at different samplings indicate that considerable quantities of nitrates were

assimilated at times. The numbers and activities of the nitrifying organisms must have kept pace with the increase in the general microscopic population.

Starkey (9) found that growing corn and oats affected the nitrifying powers of a soil to only a slight extent. Sewell (7) compared the ammonifying and nitrifying powers of corn and kafir soils and found practically no differences in the effects of the two crops. Although there were indications in these experiments that the nitrifying powers of soils may have been slightly increased under corn, wheat, and barley and decreased under kafir the differences were too small to be significant. As nitrification and nitrate assimilation occur simultaneously in a soil and there is no way of determining the extent of either or the factors involved, conclusions from small differences in the data are not justifiable.

The method used in these investigations gave no indication of the presence of inorganic phosphorus in the soil solution. The soil solutions evidently contained phosphorus available to plants, but containing active calcium did not give tests for inorganic phosphorus. If the plants excreted organic compounds containing phosphorus the amounts were exceedingly small and the tests were not sufficiently delicate to show, with any degree of accuracy, what differences may have been caused by the growing plants.

Increased numbers of microorganisms in cropped soils are indicative of increased amounts of food materials. The tests used showed no differences in the amounts of water-soluble organic matter in the soils. No accumulation of easily decomposable materials under plants would be expected, however, except under sterile conditions.

## SUMMARY

Determinations were made to ascertain the influences of the development of corn, kafir, wheat, and barley on numbers and certain activities of microörganisms in soils. Measurements were made periodically during the growth of the plants on carbon dioxide evolution; hydrogen-ion concentration of the soil solution; numbers of filamentous fungi, bacteria, and actinomycetes; nitrate content of the soils; nitrifying, nitrogen assimilating, and nitrogen fixing powers of the soils; and on the amounts of water-soluble phosphorus and water-soluble organic matter:

Wetting soils which had become more or less dry resulted in a marked evolution of carbon dioxide, the effects lasting about four weeks.

Larger amounts of carbon dioxide were produced in cropped than in uncropped soils, the largest amounts occurring when the plants were making their greatest vegetative growth.

The production of carbon dioxide was related to the growth characteristics of the plants and distinct for each of the plants.

Increased numbers of filamentous fungi were found under corn and decreased numbers under kafir, wheat, and barley. Larger numbers of bacteria and actinomycetes occurred in planted than in unplanted soils, the largest numbers being found under corn.

Increased numbers of microorganisms were not accompanied by increased evolution of carbon dioxide in fallow soils.

The plants made their largest draft on soil nitrates at the periods of maximum vegetative growth.

There were indications that the growing plants may have increased the nitrifying and nitrogen assimilating powers of the soils to a slight extent, but the differences were not significant.

Corn and kafir seem to decrease the hydrogen-ion concentration of the soil solution.

Although growing plants may produce changes in the quantities of water-soluble phosphorus and water-soluble organic matter, significant differences could not be detected by the methods used.

It appears likely that part of the increased numbers of microorganisms found under the growing plants were the result of the excretion of soluble organic matter by the growing plants.

The results obtained in these investigations indicate that conditions for microbial activities are somewhat more favorable under corn, wheat, or barley than under kafir.

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# THE LONGEVITY OF LEGUME BACTERIA ON SEED, AS INFLUENCED BY PLANT SAP[1]

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The importance of inoculating legumes with nitrogen fixing bacteria is universally recognized; and of the various methods practiced that of seed inoculation is the one most often utilized. It is customary for the farmer to inoculate the seeds immediately prior to planting. However, if bacteria can be made to survive on seedcoats for a sufficient length of time, then the seeds could be inoculated at some central point by the seed dealers, thus saving the planter much time and trouble. Besides, inoculation could then be carried out in a more uniform and economical manner.

Some studies have been conducted as to the length of time the organisms will exist on seedcoats in the presence, and in the absence, of accessory substances. Although plant juices have been utilized to grow bacteria in artificial media (3), yet no work has been reported concerning the utilization of plant sap as an aid to increase the viability and vitality of legume bacteria when these are dried on the seed.

## HISTORICAL

Results obtained by observation indicate that the symbiotic nitrogen-gathering bacteria can exist for a number of years in soil, in the absence of the host plant. Hopkins (6) states, ". . . . how long the bacteria will live in a soil without a leguminous crop upon which they feed is not definitely known. Certainly they live for two or three years, but probably not more than five or six years." According to Russell and Morrison (11) soybean nodule bacteria are capable of living under field conditions for a period of 17 years. Albrecht (1) concludes that the legume bacteria of soybeans and red clover do not remain viable longer than six years in dry soil; whereas they will persist for a longer time in a soil left under natural conditions.

The conclusions arrived at concerning the longevity of *B. radicicola* when dried in the absence of soil are far different. In 1905 (9), the U. S. Department of Agriculture distributed legume bacteria in a dried form, but these proved unsuccessful, as the organisms soon died on the dried strands of cotton. In the same year, Kellerman and Beckwith (7) showed that a culture properly dried and protected from a moist atmosphere retains its vitality for 90 days; but, when dried under atmospheric conditions, the culture became sterile in 24 days.

Chester (4), in 1907, as a result of a review of the literature concerning the effect of desicca-

[1] The author is indebted to Jessie G. Fiske for suggesting the problem, and for her helpful criticism throughout the work, and also to Dr. Arthur Stahl for compilation of preliminary data. Journal Series paper of the New Jersey Agricultural Experiment Station, department of seed analysis.

tion on bacteria, mentions that; first, the resistance to drying is increased by the thickness of the layer; second, intermittent drying, such as occurs in air, results in rapid death of the organisms; third, organisms dried at body temperature die more quickly than when dried at lower temperatures; and fourth, old and weakened cultures are less resistant to drying than the highly virulent cultures. He dried *B. radicicola* at 35°C. (a temperature far above that to which the organism is usually exposed) and he states, "*Ps. radicicola* has little power to withstand drying . . . ." As a result of his experiment with alfalfa seed, in which the seeds were sterile 18 days after drying, he says, "*Ps. radicicola* when dried on seed perish very quickly."

Temple (12), showed in 1916 that *B. radicicola* may live for months on the seed coat of cowpeas. Canada field peas were inoculated and, after drying, were stored in loosely stoppled bottles. At intervals of 30 days, seeds from this lot were planted, and nodules were found on the roots up to the fifth month of drying.

In 1919, results obtained by Fellers (5) were published. Soy-bean and alfalfa seeds, after being treated with inoculants for varying lengths of time, were carefully dried and stored in paper bags. At fixed intervals samples were tested for the presence of *B. radicicola* by means of the agar plate and by nodulation on plants grown from the seed. Organisms remained viable for at least six months, irrespective of the length of time the seeds were kept in contact with the inoculant. The greatest destruction of cells occurred during the first few hours; after this, they perished more slowly and uniformly. As gum tragacanth and similar substances do not aid greatly in keeping alive the bacteria on the seed, he does not recommend their use.

Richmond (10) inoculated seeds with muddy water prepare from soil, upon which the crop in question had been grown. He found that seeds so inoculated with muddy water from an acid soil were free of nodule bacteria within seven days, whereas seeds treated with muddy water prepared with neutral soil retained viable organisms for almost a year.

During the same year, 1926, Allicante (2) reported his results, concerning the viability of the nodule bacteria. He made a study of the effect of soil, glue, and sugar on the length of time the organisms will survive on the seed coat. Treatments containing sugar gave nodules superior in number and size to those treatments containing soil or glue. Sugar, according to this worker, protects against desiccation, because it possesses the characteristic of gathering moisture from the air; whereas, soil has a beneficial influence, because of the film of moisture surrounding the soil particles. He found that seeds stored in cloth bags maintain the life of the legume organisms for a longer period of time than when stored in glass containers. These experiments, however, were terminated at the end of two months.

In 1927, Lockhead (8) reported experiments on alfalfa seeds inoculated with a suspension of organisms in sweetened milk, as compared with inoculated sand. Seeds treated by the "skim-milk" method retained viable bacteria on their seed coats for six months, and nodulation was favored by storing the seeds at low temperatures.

## EXPERIMENTAL

Seeds of winter vetch and of sweet clover were used throughout this experiment.

*Sterilization of seeds.*—The seeds were placed in 1 to 500 solution of $HgCl_2$ for 5 minutes (5), removed and washed in four changes of sterile distilled water. When tested in bouillon tubes, 97 per cent of the seeds proved to be sterile, although no reduction in their germination was noticeable. Tests for mercury showed no trace of this element.

*Medium used for Petri dishes.*—A modified Ashby's medium was used for growing the organisms and for counting them (5). One liter of the medium contained 10 gm. mannite, 0.2 gm. $KH_2PO_4$, 0.2 gm. $MgSO_4$, 0.1 gm. $CaSO_4$, 1.0 gm. $CaCO_3$, and 18 gm. agar.

*Preparation of the inoculum.*—Twenty-five grams of washed sweet clover and winter vetch nodules were separately crushed in 500 cc. of sterile water, after which the infusions were filtered through several layers of cheesecloth. Then 0.1-cc portions were mixed with the Ashby's medium in 250-cc. Erlenmeyer flasks, and inoculated at 28°C. for 10 days. The surface colonies were removed by a minimum amount of sterile water by means of shaking and by rubbing with a sterile spatula. Like strains of the organisms were then mixed together in a sterile flask, and about 20 cc. of 25 per cent sterile sugar solution was added to each of the two flask. The contents of each flask were then divided into nine portions. The liquid in three flasks of each strain was diluted with 10 cc. of sterile water; to another set of three flasks, 10 cc. of sterile milk was added; while in the third set of three flasks, 10 cc. of plant sap was used.

*Preparation of the plant sap.*—The plant sap was obtained by compressing the plant and extracting the liquid. The plants were young and succulent, the clover being about 1 month old, and the vetch 3 weeks. The expressed juices were sterilized before being added to the inoculum.

*Reaction of the inoculum.*—The reaction of each inoculum was adjusted by means of dilute HCl and NaOH to pH 6.5, 7.0, 7.5, and verified by means of the potentiometer.

*Inoculation of the seeds.*—After the seeds had been sterilized and dried between sterile blotting paper, about 50 gm. of clover seed was put into each of the flasks containing the clover organism, and about 80 gm. of vetch seed was placed in the flasks containing the vetch organism. These were allowed to remain 30 minutes in the inoculum, then they were placed between sterile blotting paper and dried.

*Storage of inoculated seeds.*—Each treatment of the dried inoculated seeds was divided into two portions and placed in sterile cloth bags. One set of these bags was stored in the laboratory, while the other set was stored in a refrigerator at 5°C.

*Bacteriological technique.*—Fifteen vetch seeds and 200 clover seeds were removed from each of the bags by means of sterile forceps, placed in flasks containing 100 cc. sterile water, and allowed to stand for 60 minutes. These were then shaken for 5 minutes, dilutions made, and then plated on the Ashby's medium (5). The dilutions commonly used were: 1/1,000, 1/100,000 and 1/1,000,000. Each dilution was poured in duplicate and the plates were incubated at 27°–30°C. for 10 days, after which they were counted.

*Greenhouse tests.*—Two-gallon earthenware pots, containing white quartz sand, were used for the nodulation tests. Each test was run in duplicate. Each of the pots planted to vetch had 15 seeds, while those planted to clover had 200 seeds. After 40 days the sand and plants were removed and the nodules counted.

The plants were watered with a nitrogen-free solution containing the following salts per liter: 10 gm. $CaSO_4$, 4.6 gm. $KH_2PO_4$, 2.3 gm. $MgSO_4$, and 0.25 gm. $FeSO_4$.

TABLE 1

*The longevity of* B. radicicola *per 15 winter vetch seeds, and nodules per plant*

| WEEKS OF STORAGE | INOCULUM ALONE | | | | | | INOCULUM PLUS PLANT SAP | | | | | | INOCULUM PLUS MILK | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pH 6.5 | | pH 7.0 | | pH 7.5 | | pH 6.5 | | pH 7.0 | | pH 7.5 | | pH 6.5 | | pH 7.0 | | pH 7.5 | |
| | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules |
| *Seeds stored at room temperature* | | | | | | | | | | | | | | | | | | |
| 0 | 690 | 4.3 | 1,295 | 18.2 | 700 | 14.3 | 1,625 | 12.7 | 490 | 8.9 | 1,650 | 9.0 | 400 | 10.4 | 700 | 15.3 | 690 | 20.0 |
| 1 | 150 | 2.4 | 90 | 6.3 | 100 | 12.5 | 1,190 | 10.9 | 750 | 10.0 | 790 | 10.9 | 260 | 10.4 | 340 | 11.0 | 160 | 10.5 |
| 3 | 85 | 0.4 | 150 | 8.6 | 40 | 0.2 | 650 | 4.6 | 200 | 16.0 | 710 | 18.4 | 111 | 8.9 | 120 | 10.3 | 160 | 12.1 |
| 6 | 10 | 2.0 | 25 | 3.6 | 50 | 1.2 | 500 | 4.5 | 600 | 8.0 | 625 | 3.2 | 110 | 2.1 | 90 | 0.7 | 5 | 1.9 |
| 12 | 15 | 1.9 | 25 | 0 | 14 | 4.9 | 90 | 4.9 | 95 | 2.2 | 250 | 5.4 | 0 | 0.2 | 10 | 0 | 4 | 0 |
| 24 | 2 | 0 | 0 | 0 | 10 | 0 | 2 | 5.2 | 100 | 10.2 | 5 | 0 | 250 | 1.2 | 14 | 0 | 4 | 3.2 |
| 56 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| *Seeds stored at 5°C.* | | | | | | | | | | | | | | | | | | |
| 1 | 100 | 15.9 | 60 | 18.2 | 100 | 5.4 | 1,750 | 11.1 | 690 | 10.4 | 1,200 | 9.7 | 175 | 7.6 | 125 | 2.5 | 100 | 0.7 |
| 3 | 75 | 6.4 | 100 | 7.2 | 150 | 3.3 | 1,300 | 12.2 | 1,300 | 25.4 | 750 | 19.9 | 100 | 0.5 | 90 | 4.6 | 100 | 9.5 |
| 6 | 15 | 0.2 | 90 | 1.6 | 100 | 1.1 | 400 | 8.2 | 790 | 10.4 | 700 | 2.5 | 100 | 6.3 | 490 | 1.6 | 1,120 | 1.0 |
| 12 | 4 | 0.2 | 10 | 1.0 | 60 | 0.9 | 120 | 3.9 | 360 | 7.5 | 60 | 10.2 | 100 | 0 | 20 | 0.2 | 40 | 0.6 |
| 24 | 4 | 0 | 15 | 1.2 | 20 | 2.0 | 100 | 2.6 | 350 | 7.4 | 100 | 1.0 | 0 | 0 | 50 | 0.2 | 40 | 0.9 |
| 56 | 0.1 | 0 | 0.9 | 0 | 0 | 0 | 0.3 | 0 | 1.1 | 0 | 0.2 | 0 | 0 | 0 | 0.2 | 0 | 0 | 0 |

TABLE 2

*The longevity of* B. radicicola *per 200 sweet clover seeds, and nodules per plant*

| WEEKS OF STORAGE | INOCULUM ALONE | | | | | | INOCULUM PLUS PLANT SAP | | | | | | INOCULUM PLUS MILK | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pH 6.5 | | pH 7.0 | | pH 7.5 | | pH 6.5 | | pH 7.0 | | pH 7.5 | | pH 6.5 | | pH 7.0 | | pH 7.5 | |
| | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules | Colonies × 1,000 | Nodules |
| *Seeds stored at room temperature* | | | | | | | | | | | | | | | | | | |
| 0 | 560 | 2.4 | 1,275 | 1.1 | 3,162 | 6.9 | 900 | 12.9 | 1,425 | 10.0 | 3,690 | 9.4 | 280 | 11.1 | 590 | 15.9 | 160 | 16.2 |
| 1 | 265 | 6.3 | 110 | .1 | 150 | 7.3 | 725 | 10.0 | 925 | 30.2 | 430 | 20.1 | 100 | 4.0 | 350 | 2.7 | 160 | 7.6 |
| 3 | 212 | 0.3 | 75 | 1.0 | 110 | 0.5 | 150 | 10.0 | 375 | 12.0 | 100 | 4.0 | 214 | 4.4 | 110 | 5.0 | 50 | 3.1 |
| 6 | 6 | 0.1 | 15 | 3.2 | 20 | 1.2 | 190 | 2.5 | 208 | 4.1 | 122 | 5.2 | 175 | 0.2 | 100 | 1.0 | 110 | 3.2 |
| 12 | 1 | 0 | 4 | 0 | 0 | 1.2 | 15 | 0.4 | 4 | 8.1 | 8 | 2.0 | 16 | 0 | 45 | 0.8 | 120 | 1.3 |
| 24 | 1 | 1.9 | 0 | 0 | 2 | 0.4 | 25 | 4.8 | 100 | 1.2 | 90 | 1.5 | 0 | 0.4 | 260 | 0 | 500 | 1.0 |
| 56 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| *Seeds stored at 5°C.* | | | | | | | | | | | | | | | | | | |
| 1 | 350 | 2.6 | 285 | 3.8 | 590 | 9.4 | 1,125 | 10.2 | 2,200 | 15.8 | 1,100 | 7.4 | 125 | 8.7 | 130 | 0.4 | 110 | 10.5 |
| 3 | 230 | 0 | 345 | 3.2 | 115 | 6.2 | 750 | 15.0 | 1,600 | 8.0 | 275 | 10.0 | 140 | 0.3 | 250 | 0.8 | 125 | 2.0 |
| 6 | 50 | 0.2 | 120 | 5.6 | 30 | 2.4 | 390 | 4.5 | 750 | 6.4 | 1,360 | 3.9 | 100 | 1.0 | 125 | 1.8 | 30 | 4.5 |
| 12 | 10 | 0.9 | 78 | 1.0 | 105 | 1.2 | 340 | 8.9 | 1,000 | 2.2 | 942 | 4.4 | 48 | 0.4 | 60 | 0 | 40 | 2.3 |
| 24 | 5 | 0.5 | 70 | 0.8 | 90 | 1.0 | 250 | 7.2 | 40 | 6.0 | 195 | 1.5 | 60 | 0.6 | 60 | 2.6 | 75 | 0 |
| 56 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 1.7 | 0 | 0.1 | 0 | 0 | 0 | 0.3 | 0 | 0.1 | 0 |

## PROCEDURE

Immediately after the seeds were inoculated and dried, they were tested for the number of viable organisms, and another set was planted in the pots for nodule counts.

The seeds were then stored in the manner indicated, and tests for bacteria and for nodule counts were made at the end of 1, 3, 6, 12, 24, 56, and 78 weeks. The results are presented in tables 1 and 2.

The number of nodules per plant is calculated from the seeds that germinated and grew.

## DISCUSSION

The data presented in the tables indicate that the addition of plant sap to the inoculum assures the preservation of a larger number of viable organisms on the seed than is possible with the use of milk or water. Although, at the end of 24 weeks, positive results were obtained from almost all the treatments, yet it is obvious that the inoculum plus plant sap gave the greatest number of bacteria and also the highest degree of nodulation. At the 56-week period, no nodule bacteria could be found on the seeds stored at room temperature; while those seeds treated with plant sap or with milk, and placed at 5°C. showed a few of the organisms. The former gave slightly higher results, but no nodules could be found on the plants grown from these seeds. As only certain cells of *Bacillus radicicola* have the power to penetrate the root and produce nodules, there must be a minimum number of these organisms present on the seed, for Thornton and Ganzulee (13) have shown that the degree of nodulation is closely associated with a predominance of the coccoid or motile form of *B. radicicola*. The increased nodulation which occurs with the addition of plant sap for shorter storage periods may be caused by the greater activation of these coccoid forms.

The differences in the reaction of the inoculum are so slight that nothing definite can be concluded; yet it appears that pH 7 gives the best result. Wilson (14), noting that ageing of seed is accompanied by a change in reaction, as a result of respiration, believes this increase in acidity may have some bearing on the longevity of legume bacteria on the seed.

If the rate of mortality due to desiccation is constant (5), then nodulation could be expected after the 24-week period, especially in the seeds treated with plant sap. However, the inoculation of the seed, and its subsequent storage, must be carefully controlled in order to assure a fair degree of nodulation after a period of time.

## SUMMARY

Vetch and clover seeds were sterilized and kept for 30 minutes in contact with their specific inoculum, after which they were dried and stored, some at room temperature, and the remainder at 5°C.

The organisms on seeds inoculated with inoculum containing plant sap from

their specific plants withstood desiccation to a higher degree than organisms on seeds similarly treated with inoculum containing milk.

The slight differences in the reaction, pH 6.5, 7,7.5, as used in this experiment had but little effect on the viability of the legume bacteria.

Refrigeration of seeds inoculated with *B. radicicola* increased the longevity of the organisms attached to the seed coat.

Although seeds treated with plant sap retained viable bacteria in fairly large numbers until the twenty-fourth week, yet such storage for seeds so inoculated is not recommended at this time.

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